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USSR AND EASTERN EUROPE SCIENTIFIC ABSTRACTS

CHEMISTRY

No. 59

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USSR

UDC 547.944/945

ISONITRAMINE -- A NEW ALKALOID FROM NITRARIA SIBIRICA

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 5, 1977 pp 720-721
manuscript received 27 Jun 77

OSMANOV, Z., IBRAGIMOV, A. A. and YUNUSOV, S. YU., Institute of Plant Chemistry, Academy of Sciences, Uzbek SSR

[Abstract] Extraction of the above-ground portion of *Nitraria sibirica* yielded 0.25% total alkaloids. A benzene solution of the ether nonphenolic portion was separated with buffer solutions from pH 8 to 4 at intervals of 1. Treating the pH 8 fraction, the authors produced a white, crystalline, optically active base with $[\alpha]_D^{30}$, mp 102-103 C, called isonitramine. The molecular weight, UV, IR and NMR spectra confirm the structure of the new base, which has substituents in the same position as in nitramine, although the new base is doubtless different from nitramine, as confirmed by the different physical state, direction, and magnitude of optical rotation and chemical effects. References 4: 2 Russian, 2 Wester.

USSR

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NEW ALKALOIDS OF UNGERNIA SPIRALS

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 5, 1977 p 719 manuscript received 27 Jun 77

KADYROV, KH. A., ABDUSAMATOV, A. and YUNUSOV, S. YU., Institute of Plant Chemistry, Academy of Sciences, Uzbek SSR; Tashkent Agricultural Institute

[Abstract] Data are presented on the structure of the previously reported alkaloids, ungsiroline and ungsirolidine, on the basis of UV, NMR, and mass spectra, ungsiroline is des-N-methylepipimacronine, while ungsirolidine is dihydroungsiroline. References 4: 1 Russian, 3 Western

USSR

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ALKALOIDS OF AMMODENDRON KARELINII

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 5, 1977 pp 1717-1718
manuscript received 6 Jun 77

KUSHMURADOV, YU. K., ASLANOV, KH. A. and KUCHKAROV, S., Tashkent State
University

[Abstract] The plant *Ammodendron karelinii* Fisch. et Mey. was studied, and 2 kg of air-dried leaves yielded 37 g of alkaloids by methanol extraction. The bases were separated by successive extraction with an alkaline solution of petroleum ether, benzene and chloroform. The primary alkaloid of the plant, pachycarpine, was separated as the hydriodide (25 g) from a petroleum ether fraction. A number of other alkaloids were found in the other fractions including pachycarpine N₁₆-oxide. References 3: all Russian.

USSR

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O-ACETYLDELECTINE -- A NEW ALKALOID FROM DELPHINIUM DICTYOCARPUM

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 5, 1977 pp 1716-1717
manuscript received 10 May 77

SALIMOV, B. T., YUNUSOV, M. S. and YUNUSOV, S. YU., Institute of Plant
Chemistry, Academy of Sciences, Uzbek SSR

[Abstract] Continuing a study of the alkaloids of the above-ground portion of *Delphinium dictyocarpum* DC, a new base, C₃₃H₄₆O₉N₂, mp 118-120C (methanol) was separated. IR and NMR spectral data are presented, which show that the new base is 10-O-acetyldelectine. A structural formula is presented. References 5: 4 Russian, 1 Western.

USSR

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THE ALKALOIDS OF LIRIODENDRON TULIPIFERA

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 5, 1977 pp 1715-1716
manuscript received 10 May 77

ZIYAYEVA, R., YUNUSOV, M. S. and YUNUSOV, S. YU., Institute of Plant Chemistry,
Academy of Sciences, Uzbek SSR

[Abstract] In a continuation of a study of the alkaloid composition of various organs of the plant *Liriodendron tulipifera* L, the nonphenol ether portion of

the total of alkaloids was separated in a column of silica gel. A new base, $C_{19}H_{17}NO_3$, mp 143-145°C (benzene), optically inactive, easily soluble in ordinary organic solvents, was detected. UV and NMR spectra data are presented which show that the new base is dehydroisolaureline. A structural formula is presented. References 11: 3 Russian, 1 Bulgarian, 7 Western.

USSR

UDC 547.943

ORIPAVIDINE -- A NEW ALKALOID FROM PAPAVER ORIENTALE

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 5, 1977 p 714
manuscript received 29 Apr 77

ISRILLOV, I. A., DENISENKO, O. N., YUNUSOV, M. S., YUNUSOV, S. YU., and MURAV'YEVA, D. A., Institute of Plant Chemistry, Academy of Sciences, Uzbek SSR; Pyatigorsk Pharmaceutical Institute

[Abstract] A new base has been separated from the phenol portion of the total alkaloids of *Papaver orientale* L: $[\alpha]_D -90^\circ$; Oripavidine decomposes at 215°C. It is easily soluble in methanol, ethanol and alkalies, and slightly soluble in ether, benzene, chloroform, pyridine and hexane. UV, IR and NMR spectral data are presented, indicating that Oripavidine is a morphanine alkaloid with the structure of N-dimethyloripavine. References 2: Western.

USSR

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SCOPOLIA TANGUTICA ALKALOIDS

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 5, 1977 pp 712-713
manuscript received 3 Mar 77

MININA, S. A., ASTAKHOVA, T. V. and FESENKO, D. A., Leningrad Chemical-Pharmaceutical Institute

[Abstract] Two new alkaloids in addition to hyoscyamine and scopolamine, were separated from the above-ground portion of *Scopolia tangutica* Maxim grown in Leningradskaya Oblast by adsorption column chromatography and selective elution: base I with R_f 7.45, and 0.41, and base II with R_f 0.34 and 0.55. Molecular weights, mass spectra and reactions are given for the two substances. It is concluded that I is an ester of scopine and α -phenyl- α,β -dihydroxypropionic acid and is identical in structure anisodine. II has the structure of 6-hydroxyhyoscyamine separated earlier from *Physochlaina dubia* and detected chromatographically in *S-tangutica* grown in China. References 5: 2 Russian, 3 Western.

USSR

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VINCA ALKALOIDS

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 5, 1977 pp 597-617
manuscript received 6 May 77

MALIKOV, V. M. and YUNUSOV, S. YU., Institute of Plant Chemistry, Academy of Sciences, Uzbek SSR

[Abstract] Of the eight known species of Vinca, 117 alkaloids have been separated. The name, chemical structure and species of Vinca from which they are obtained are given for each alkaloid (the structures of 13 bases have not yet been determined, and they are not included). The alkaloids are divided into four groups: derivatives of indol, indolin, oxiindol and indolenine. Comparative data are presented on the distribution of these groups of compounds in the eight species of Vinca most commonly found. Characteristic reactions, spectral data and some chemical transformations of the alkaloids are analyzed. The possible biogenetic interactions and mutual transformations among bases which are in the four classes mentioned above are discussed. Information confirming these suggestions is presented.

USSR

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INDOLE ALKALOIDS OF A CALLUS CULTURE OF VINCA ROSEA

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 3, 1977 p 429 manuscript received 22 Feb 77

ANDREYEVA, T. I. and BEREZNEGOVSKAYA, L. N., Tomsk Medical Institute

[Abstract] Contradictory information has been published concerning the capability of the callus tissue of vinca rosea to synthesize alkaloids. Callus tissue obtained by the authors in 1974 was grown on a modified medium in darkness at -270°C and 70% relative humidity. Conventional methods were used to prove the capability of the tissue to synthesize indole alkaloids. The yield, depending on the origin of the tissue and growing time, is 0.10-0.20% total alkaloids. Spectra data are presented. Five individual substances were separated by chromatography on a column filled with inactivated aluminum oxide and subsequent preparative separation on "silufo1" plates. The substances were identified as ajmalicine, cataranthine, vindoline, lochnericine and vinblastine. No other alkaloids were obtained in pure form and identified. References 5: Western.

USSR

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NEW ALKALOIDS OF CORYDALIS LEDEBOURIANA

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 3, 1977 pp 428-429
manuscript received 15 Feb 76

ISRATLOV, I. A., YUNUSOV, M. S., and YUNUSOV, S. YU., Institute of Plant Chemistry, Academy of Sciences Uzbek SSR

[Abstract] Continuing the separation of the total alkaloids of the above-ground portion of corydalis ledebouriana collected in Tashkentskaya Oblast, the authors separated two new bases. Base I, m.p., 219-220C $[\alpha]_D + 0C$, has the composition $C_{21}H_{23}O_6N$. Base II, m.p. 140-141C, $[\alpha]_D + 114C$, called by the authors ledebouridine, has the composition $C_{20}H_{21}O_6N$. Spectral data are presented. Ledebouridine is considered a spirobenzylisoquinoline alkaloid containing two hydroxyl groups in a five-membered ring. A structural formula is suggested. References 4: 1 Russian; 3 Western.

USSR

UDC 547.944/945

HAPLAMIDINE - A NEW ALKALOID FROM HAPLOPHYLLUM LATIFOLIUM

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 3, 1977 p 427
manuscript received 11 Feb 77

NESMELOVA, YE. F., BESSONOVA, I. A., and YUNUSOV, S. YU., Institute of Plant Chemistry, Academy of Sciences Uzbek SSR

[Abstract] Continuing their study of the alkaloids of haplophyllum latifolium, the authors studied the above-ground portion of the plant collected in the blossoming phase on 26 May 1975 on Fergana Ridge, Kirg SSR. The evaporated methanol extract from 7 kg of the plant was partially extracted with chloroform, treated with 4% alkali and the neutral fraction remaining in the chloroform after distillation of the solvent chromatographed on aluminum oxide, and on silica gel. Ether eluates subsequently yielded a new alkaloid called haplamidine, a white crystalline substance with the composition $C_{20}H_{22}N_2O_2$, m.p. 139-140 C, with no basic properties, poorly soluble in organic solvents, insoluble in water, dilute acids and alkali. Spectral data are presented. A structural formula is suggested. The data indicates that the structure is N-cinnamoyl-N'-benzoyltetramethylenediamine. References 4: 3 Russian; 1 Western.

USSR

UDC 547.944/945

ALKALOIDS FROM UNGERNIA SPIRALIS

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 3, 1977 p 426
manuscript received 2 Feb 77

KADIROV, KH. A., and ABDUSAMATOV, A., Institute for Plant Chemistry, Academy of Sciences Uzbek SSR; Tashkent Agricultural Institute

[Abstract] Separation according to strength of basicity of the ether total of alkaloids from the roots of *ungernia spiralis* collected on 25 May 1974 in the Turkmenian SSR near Karakalinsk yielded licorine and tacettine plus a new base with the composition $C_{18}H_{21}NO_5$, m.p. 98-99 C, $[\alpha]_D^{20} + 10.7C$ [I] and a base with the composition $C_{17}H_{19}NO_5$, m.p. 148-149 C, $[\alpha]_D^{20} + 105 C$ [II] and a base with the composition $C_{17}H_{21}NO_5$, m.p. 142-143 C, $[\alpha]_D^{20} + 11 C$ [III]. Comparison of spectral data indicates that I may be dihydroepimacronine. References 4: 3 Russian; 1 Western.

USSR

UDC 547.944/945

TRIACETYLGLYCOPERINE - A NEW ALKALOID FROM HAPLOPHYLLUM PERFORATUM

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 3, 1977 pp 425-426
manuscript received 2 Feb 77

ABDULLAYEVA, KH. A., BESSONOVA, I. A., and YUNUSOV, S. YU., Institute for Plant Chemistry, Academy of Sciences Uzbek SSR

[Abstract] Continuing the study of the alkaloids of the methanol extract of *haplophyllum perforatum*, the authors have discovered a new base with the composition $C_{25}H_{27}NO_{11}$, m.p. 181-182 C, $[\alpha]_D - 91C$, easily soluble in chloroform, acetone, dilute acids, less soluble in ether, petroleum ether, insoluble in water and alkalis. The individuality of the substance was tested in several systems of solvents. IR and NMR spectra are similar to those presented in the literature for triacetylglycoperine. Direct comparison with a specimen of triacetylglycoperine prepared from glycoperine showed that the substances are identical. References 4: 3 Russian; 1 Western.

ALKALOIDS OF RESEDA LUTEA

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 3, 1977 pp 424-425
manuscript received 21 Jan 77

NAKHATOV, I. K., TADZHIBAYEV, M. M., MALIKOV, V. M., and YUNYSOV, S. YU.,
Institute of Plant Chemistry, Academy of Sciences Uzbek SSR

[Abstract] Alcohol extraction of the above-ground portion of *reseda lutea* (one of the *Resedaceae*) collected in Samarkand during the fruition stage yielded 0.02% total alkaloids. Chromatographic separation on a column filled with silica gel yielded a new base called lutenine, a white crystalline substance with m.p. 185-187 C composition $C_8H_7NO_2$. A structural formula is presented indicating that it is a cyclic carbamate. When heated with 10% hydrochloric acid in a water bath for 6 hours, a crystalline substance with m.p. 106-108 C was produced, having the physical and chemical properties of hydroxybenzylamine. Thus, lutenine is a 2-oxo-dihydro-1,3-benzoxazine. References 4: Russian.

ALKALOIDS OF PAPAVER ARENARIUM AND P. COMMUTATUM

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 3, 1977 p 424
manuscript received 18 Jan 77

MNATSAKANYAN, V. A., MANUSHAKYAN, M. A., and MESROPYAN, N. YE., Institute
for Fine Organic Chemistry, Yerevan

[Abstract] Methanol extraction of a dried and ground preparation of *papaver arenarium* collected in July of 1974 near Lake Sevan, produced a yield of 0.13% alkaloids. Separation of the non-phenolic portion on a column containing neutral aluminum oxide and benzene elution produced 0.025% of a base identified with macrostomine. From *papaver commutatum* Fisch. et Mey. collected in July 1975 at an altitude of 2,300 m near Krasnosel'sk, Armenia, the methanol extract produced 0.035% total alkaloids. Precipitation as hydrochlorides from the phenol portion yielded isocoridine (0.01%) from the nonphenolic portion - d-remerine (0.012%). References 4: Russian.

USSR

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BISBENZYLISOQUINOLINE ALKALOIDS

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 4, 1977 pp 451-484
manuscript received 15 Mar 77

TOLKACHEV, O. N., NAKOVA, YE. P. and YEVSTIGNEYEVA, R. P., All-Union Scientific Research Institute of Medicinal Plants, Moscow Order of the Labor Red Banner Institute of Fine Chemical Technology imeni M. V. Lomonosov

[Abstract] The authors review the state of the art of structural analysis of bisbenzylisoquinoline alkaloids. Currently, more than 150 are known. The discovery of some biologically active agents and the introduction of instrumental methods of analysis intensified research in this area. These alkaloids are classified by the number of ether linkages and their locations, except for some, where a carbon-carbon bond unites the benzyl radicals. The chemical methods of structure analysis are based on the breakdown to simpler fragments which can then be identified. A series of such reactions is being reviewed. In addition, the methods of IR and UV spectroscopy, the ORD and circular dichroism measurements have also been used in identification of structures as well as the determination of proton magnetic resonance and mass-spectroscopic analysis. These alkaloids act as myorelaxing agents. References 191: 29 Russian, 2 Bulgarian, 1 Hungarian, 159 Western.

USSR

UDC 547/945

BUXUS HYRCANA ALKALOIDS. ISOLATION OF BUXPIINE AND OF THE BASE II

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 4, 1977 pp 582-583
manuscript received 14 Apr 77

ORAZMURADOV, G. M. and ALIYEV, A. M., Azerbaydzhan State Medical Institute imeni N. Narimanov; Baku Institute of Chemistry, Academy of Sciences TSSR

[Abstract] Alkaloids extracted from the leaves of Buxus hyrcana Pojark were chromatographed on aluminum oxide column yielding buxpiine, - m.p. 171-172° (benzene) $[\alpha]_D^{24} + 157^\circ$ and a novel alkaloid, - m. p. 318-320°, $[\alpha] - 316^\circ$. References 7: 4 Russian, 3 Czech.

SOPHORA ALOPECUROIDES ALKALOIDS

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 4, 1977 pp 541-544
manuscript received 4 Mar 77

KUCHKAROV, S., KUSHMURADOV, YU. K., ASLANOV, KH. and SADYKOV, A. S., Tashkent
Order of the Labor Red Banner State University imeni V. I. Lenin

[Abstract] Two new alkaloids were isolated from *Sophora Alopecuroides* collected along the Zerevshan river during the fruit ripening period. One of these alkaloids had the formula $C_{15}H_{22}O_2N_2$, m.p. 68-70° (ether), $[\alpha] + 275^\circ$; this material was investigated in detail in an attempt to determine its structure. On the basis of UV, PMR and mass-spectroscopic data the compound was assigned the structure of the N-oxide of 13,14-dehydrosaphoridine. References 10: all Russian.

USSR

UDC 543.8:543.544

APPLICATION OF METHYLATION REACTIONS FOR THE GAS CHROMATOGRAPHIC ANALYSIS OF ORGANOPHOSPHORUS PESTICIDES

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 9, pp 1790-1795 manuscript received 31 Mar 76

NESTEROVA, I. P., All-Union Scientific-Research Institute of Biological Methods of Plant Protection

[Abstract] The difficulties inherent in the gas chromatographic (GC) analysis and the short-comings of some previous attempts are considered as a justification for the development of a new method. The pesticide Sayfos (0,0-dimethyl-S-(4,6-diamino-1,3,5-triazin-2-yl)-methyldithiophosphate) was analyzed in both known standards and in plant tissue using base hydrolysis and subsequent methylation with diazomethane. Intermediate products, reaction conditions and analytical procedures for both thin layer and gas chromatography are given. The lower detection limit for Sayfos in plant tissue is 0.04 mg/kg, based on the extraction of the pesticide with acetone, its hydrolysis and methylation and its analysis as the trimethyl thiolphosphate. References 15: 9 Western, 6 Russian.

USSR

UDC 632.95.028:543.544.42

DETERMINATION OF THE RESIDUES OF ORGANOPHOSPHORUS PESTICIDES BY MEANS OF THIN LAYER CHROMATOGRAPHY AND ENZYMATIC SPOT DETECTION

Moscow KHIMIYA V SEL'SKOM KHOZYAYSTVE in Russian Vol 15, No 7, 1977 pp 46-48

LESHCHEV, V. V., and TALANOV, G. A., All-Union Scientific Research Institute of Veterinary Sanitation

[Abstract] A simplified method for the determination of residual amounts of organophosphorus pesticides (OPP) has been proposed. The procedure involves extraction of OPP with acetone, purification of the extracts, activation of thione phosphates with hydrogen peroxide and chromatography on silica-starch thin layer plates. The plates are developed in a mixture of acetone with benzene, hexane and chloroform. To develop the spots, a chromatographic paper saturated with a solution of bromothymol blue and acetylcholine chloride is placed over the TLC plate. Quantitative analysis of the spots is performed visually by comparison against standard solutions developed in parallel. In case of unknown test samples, the identification is made from the R_f and R_c determined against a standard solution of metaphos. The sensitivity of this procedure is in the range of 0.1-0.5 μ g per test sample of standard pesticide solutions. No figures, references 24: 7 Russian, 17 Western.

USSR

UDC 541.182.2/3:632.6/7

THE PROBLEM OF OPTIMIZATION OF AEROSOL TECHNOLOGY OF APPLICATION OF PESTICIDES AND THE CONTROL OF HARMFUL INSECTS

Novosibirsk IZVESTIYA SIBIRSKOGO OTDELENIYA AKADEMII NAUK SSSR - SERIYA
KHIMICHESKIKH NAUK in Russian No 3, May 77 pp 30-47

KUTSENOGII, K. P., Institute of Chemical Kinetics and Combustion, Siberian
Affiliate, Academy of Sciences USSR

[Abstract] A review of experimental and theoretical studies on the influence of particle size on effectiveness of the application of insecticide aerosols shows that there is an area of optimal particle size for both flying and crawling insects, which could minimize poison consumption for a given insect death rate. The factors involved are analyzed and a simple mathematical model is used to produce a quantitative estimate of the scale effect. Comparison of the estimates produced with available experimental data shows that the use of particles of the optimal size can significantly reduce the consumption of pesticide in comparison to the normal recommended dose which, in addition to improving the economics of chemical pest control, can greatly (by as much as hundreds of times) decrease the residual level in plants and in the soil, and also minimize the harmful aftereffects on useful entomofauna. The mathematical model assumes that the lethal dose of insecticide is not altered by the path of administration of the insecticide to the insect and that the variation in concentration of insecticide with time need not be known; it is sufficient to know the concentration integral for the time during which the cloud of insecticide passes a given point. The ultimate determination of optimal particle size is a compromise between the minimum particle size which will precipitate through the air sufficiently rapidly and the requirement that each particle or droplet of insecticide contain a sufficient dose to kill one insect. References 57: 31 Russian, 26 Western.

USSR

UDC 66.067.322:66.074.15

AEROSOL FILTERS FOR FINE FILTRATION OF FOG

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 8, 1977 pp 614-616

NAKHUTIN, I. YE., ZAKHAROV, M. I., SOKOLOV, V. N., NOVOSELOVA, M. P.,
SEVASTVYANOV, F. N. and NIKOLAYEVA, YE. S.

[Abstract] Fiber-type fog traps (self-cleaning filters) have come into use in the USSR and abroad in the past 10 or 15 years. The operating principle of these filters is that fog particles which precipitate in the filter layer are continually removed from it under the influence of a stream of air and the force of gravity. Filters with mean fiber diameters of 5-30 μm are most common. The results of the present studies have indicated that another method

of filtration of fog with fine-fiber filters is possible, assuring high effectiveness of filtration of fog with fine-fiber filters is possible, assuring high effectiveness of filtration with low aerodynamic drag. When this method is used, the filter element is placed vertically, with the lower portion of the filter immersed in liquid. If the filter element is tall enough, most of the filter spaces are not filled with the liquid by capillary action. Self-cleaning filters based on ultrafine glass fiber with an average diameter of 2-4 μm , layer thickness 6-8 mm and height of 500 mm have resistances on the order of 50-70 to 300-400 mm water with an effectiveness of 99.9% for fog particles with median mass diameter 0.8-1.0 μm at up to 1,000 m^3/m^3 with airspeeds of 2-3 cm/s. An industrial series of filters, FARTOS filters, has been produced based on the results of these studies, and experimental use has shown good results. References 4: all Russian.

USSR

UDC 547+577.1

ADSORPTION IMMOBILIZATION OF LACTATE DEHYDROGENASE ON SILICA GEL TREATED WITH CHOLESTEROL

Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA in Russian No 5, Jul/Aug 77 pp 379-383
manuscript received 9 Dec 76

MITROFANOVA, A. N., CHUKHRAY, YE. S., PRYAKHIN, A. N., POLTORAK, O. M., Moscow University, Department of Physical Chemistry

[Abstract] A study was made of the chemical and physical properties of lactate dehydrogenase (LDH) adsorbed on silica gel treated with cholesterol. Both the absorption and desorption points fall along the same curve indicating that the adsorption is reversible. The free energy of adsorption was -8.45 kcal/mole. A comparison was made of changes in the reaction rates of LDH in solution and in the adsorbed state with changes in concentration of the enzyme, the substrate, pH, and the Michaelis constant in relation to the degree of surface coverage by the enzyme. Adsorption onto a surface significantly changes the kinetic parameters of the LDH in relation to its dissolved state. Within the range of surface coverage studied, the conversion of sodium pyruvate into lactate in the presence of LDH and NADH is limited by the diffusion of the substrate into the pores of the support. Other free energy values and several equilibrium constants are derived for specific systems. References 5: Russian.

USSR

UDC 576.1

SYNTHESIS OF NUCLEOTIDYL-OLIGONUCLEOTIDYL-(P → N)-LYSINES AND THEIR IMMOBILIZATION ON SEPHAROSE

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 3, 1977 pp 435-436
manuscript received 31 Dec 76

YUODKA, B., LIORANCHAITTE, L., LEIMONTAITE, R., MALINAUSKAS, A., KULIS, YU., SOKOLOVA, N. I., and SHABAROVA, Z. A., Vil'nyuss State University, Institute of Biochemistry, Academy of Sciences, Lithuanian SSR; Moscow State University

[Abstract] A study was made of the synthesis of alpha- and epsilon-lysine phosphoamides of nucleotides and dinucleoside phosphate, as well as immobilization of the compounds produced on sepharose by means of the lysine group. Spectral data are presented. It was found that the esters of nucleotidyl- and oligonucleotidyl-(P → N)-lysines are immobilized practically identically well through the alpha and epsilon amino groups of the lysine. Compounds with free carboxyl groups are less effectively immobilized. References 9: 4 Russian; 5 Western.

USSR

ADSORPTION IMMOBILIZATION OF ENZYMES AND THE PROBLEMS OF THE ASSOCIATION OF PROTEINS. SPECIFIC CATALYTIC ACTIVITY EXPRESSED AS A FUNCTION OF ENZYME CONCENTRATION SHOWS AN INFLECTION POINT

Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA in Russian Vol 18, No 3, May/Jun 77
pp 251-268 manuscript received 1 Feb 77

POLTORAK, O. M. and PRYAKHIN, A. N., Chair of Physical Chemistry

[Abstract] The authors propose a new method for solving many kinetic problems. The task is narrowed down to the description of various physical properties of the enzymes which, depending on the concentration of protein, could be expressed by a curve with an inflection point. Theoretical analysis of this situation requires many calculations, which can be simplified considerably in practical application by the use of tables of special functions reported in the paper. As an example for discussion, the authors analyzed the peroxidase activity of the cytochrome, expressed as a function of the degree of the carrier surface being filled with protein under conditions excluding diffusional effects. Qualitative explanation states that two groups of associates exist on the surface of the carrier having different levels of specific activity, so that when the surface concentration of the enzyme is altered, the fraction of the protein in these states will also change. Three basic models for protein association have been analyzed theoretically. Figures 3; references 2: both Russian.

USSR

UDC 577.15.022+577.158.429

STUDY OF IMMOBILIZED FORMATE DEHYDROGENASE UNDER UNSTEADY CONDITIONS IN AN IDEAL-MIXING FLOW REACTOR

Moscow BIORGANICHESKAYA KHIMIYA in Russian No 11, 1977 pp 1560-1568 manuscript received 31 Mar 77

RODIONOV, YU. V., VALEYEV, N. N., KISELEVA, Z. L., and BEREZIN, I. V., Moscow State University imeni M. V. Lomonosov; Kazan' Chemico-Technological Institute imeni S. M. Kirov

[Abstract] A method has been proposed for measuring the kinetic parameters catalyzed by immobilized enzymes, which provides the possibility for conducting calculations of the Michaelis constant K_m and the maximum reaction rate V_{max} on the basis of a single experiment. The procedure is based upon continuous registration of the reaction product concentration during the use of an ideal-mixing flow reactor under unsteady conditions. The proposed procedure was used for studying the kinetic parameters of a two substrate reaction catalyzed by NAD-dependent formate dehydrogenase immobilized on porous glass. Figures 8; references 12: 7 Russian, 5 Western.

OBTAINING FROM SECONDARY CELLULOSE ACETATE FIBERS THAT CONTAIN AN IMMOBILIZED UREASE ENZYME

Moscow KHIMICHESKIYE VOLOKNA in Russian No 4, 1977 pp 39-40 manuscript received 17 Jul 76

SEDOV, A. A., VIRNIK, A. D., YAKOVLEV, V. A., and ROGOVIN, Z. A.

[Abstract] The experiment sought to include the enzyme in the acetate fiber structure by forming it from a spinning solution where the organic solvent was in contact with the enzyme. Two variants were tested, one containing 7.6% secondary cellulose acetate in methylene chloride and ethanol (95:5), and the other with 18% secondary cellulose acetate. The variants contained, respectively, 28.8 mg/ml and 57.6 mg/ml of the enzyme. Fibers were formed in a water precipitation bath and then washed with distilled water and retained in 0.1 mole phosphate buffer at 4°C. Greater immobilization was achieved in an acetone--water solution of 93:7 than in methylene chloride. The enzyme activity of variant two did not change when the fibers so obtained were used in urea hydrolysis or during preservation at 4°C. References 9: 5 Russian, 4 Western.

USSR

UDC 541.183.12:547.1'118

ION EXCHANGE RESINS HAVING GROUPINGS OF N-METHYL-ALPHA-AMINO-2-FURYL-METHYLPHOSPHONIC ACID AND ITS DIETHYL ETHER

Moscow IZVESTIYA AKADEMII NAUK SSSR--SERIYA KHIMICHESKAYA in Russian No 8, 1977 pp 1861-1863

BELOV, YU. P., DAVANKOV, V. A., and ROGOZHIN, S. V., Institute of Organoelemental Chemistry, USSR Academy of Sciences

[Abstract] Amination of the chloromethylated polystyrene skeleton with the diethyl ester of N-methyl-alpha-amino-2-furylmethylphosphonic acid yielded an ion exchange resin. When the ester residues of this ion exchange resin were cleaved, an amphotite was produced which contained N-methyl-alpha-amino-2-furylmethylphosphic acid groups. The ester groups of the ion exchange resin were cleaved with anhydrous HCl. The reaction was conducted in absolute dioxane with moderate heating (50-85°) until no more C₂H₅Cl was given off. The amphotite was found to swell most in acid, and least in water and in alkaline media. Sorption of the ions Fe³⁺, Cu²⁺, Ni²⁺, Zn²⁺ and Cd²⁺ by the ion exchange resin was limited: Fe³⁺ and Cu²⁺ were sorbed most strongly. The differing strengths of the sorption complexes suggest that the ion exchange resins may be used for the selective sorption of metals from acid solutions. References 15: 8 Russian; 7 Western.

USSR

UDC 547.754'831.3'892.07

ACETALS OF ACID LACTAMS AND AMIDES. 20. SYNTHESIS OF HYDROGENATED DERIVATIVES OF INDOLE, QUINOLINE AND 1H,1-BENZAZEPINE

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian No 10, Oct 77
pp 1348-1351 manuscript received 10 Jan 77

GRANIKM, V. G., SHIDKOVA, A. M., GLUSHKOV, R. G., GRIGOR'YEV, A. B.,
POLIYEVKTOV, M. K., VLASOVA, T. F. and ANISIMOVA, O. S., All-Union
Scientific-Research Chemical-Pharmaceutical Institute imeni S. Ordzhonikidze

[Abstract] Reaction of 1-methyl-2-benzoylmethylenepyrrolidine, -piperidine and -hexahydroazepine with acryloyl chloride followed by treatment of the reaction mixture with triethylamine yielded hydrogenated derivatives of indole, quinoline and 1H,1-benzazepine. Alkylation of 1-methyl-5-keto-8-benzoyl-1,2,3,4,5,6,7,8-octahydroquinoline with triethyloxonium fluoroborate followed by treatment with sodium ethoxide leads to the respective acetal which, upon reaction with substituted anilines yields 1-methyl-5-acylimino-8-benzoyl-1,2,3,4,5,6,7,8-octahydroquinolines. The IR and PMR spectra of these novel products are presented. References 6: 2 Russian, 4 Western.

USSR

UDC 547.759.3'73.07

SYNTHESIS OF DIHYDROTHIENO[3,4-b]INDOLES

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian No 10, Oct 77
pp 1327-1331 manuscript received 4 Jan 76, revised 7 Feb 77

KOGAN, N. A., Leningrad Chemical-Pharmaceutical Institute

[Abstract] A novel heterocyclic system, 3-imino-4-methyldihydrothieno-[3,4-b]indole, was synthesized by reacting the thioamide of 1-methyl-indole-2-carboxylic acid with aldehydes or ketones in alcohol, ether or acetic acid and in presence of hydrogen chloride. This reaction does not take place with complex ketones. The imino group of the thiene cycle was saponified and acetylated; reaction with Li AlH_4 cleaved the thiene ring yielding indolylphenylmethyl sulfide. The proposed reaction mechanism included an addition of the thioamide SH group to the carbonyl compound as the first step, followed by intramolecular cyclization through the 3-position of indole. Figure 1; references 3: all Russian.

INDOLE DERIVATIVES. LXI. 5,7,8,13b-TETRAHYDRO-13H-BENZ(g)INDOLO(2,3-a)
INDOLIZINES

Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian Vol 30, No 7, 1977
pp 607-610 manuscript received 12 May 77

POGOSYAN, S. A., TERZIAN, A. G. and TATEVOSYAN, G. T., Institute of Fine
Organic Chemistry imeni A. L. Midzhoyan, Academy of Sciences ArmSSR

[Abstract] Imides of cyclohexene-cis-1,2-dicarboxylic acid are readily reduced to hydroxyimides by lithium aluminum hydride (LAH). Therefore an investigation was made of the feasibility of analogous reduction of imides that have the aromatic ring E in their structure. Such imides are usually reduced in methanol in the presence of ammonium chloride. The authors show that LAH is a more effective reducing agent. When LAH is used, purer hydroxyimides III are obtained with higher yields in all cases.



I

II

Ia, IIa, R = -C₆H₅; I6, II6, R = -C₂H₅

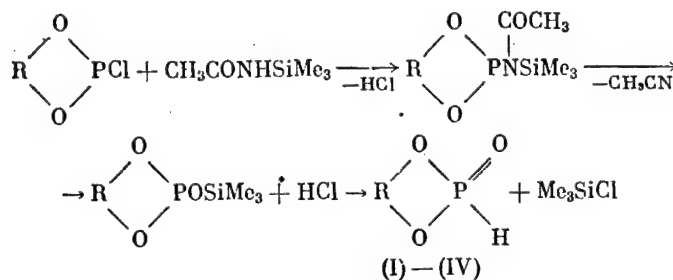
The initial components were triptamine, α-methyltriptamine and phthalic anhydride. Imides II were converted by LAH in tetrahydrofuran to hydroxyimides III, which were then cyclized to lactams IV. The lactams were reduced to bases I by LAH in tetrahydrofuran. A pharmacological study of base I with R = CH₃ showed that it is not analgesic in experiments on white mice in a dose of 50 mg/kg. References 5: 3 Russian, 2 Western.

NEW METHOD FOR SYNTHESIZING ACIDS OF CYCLIC PHOSPHITES

Moscow IZVESTIYA AKADEMII NAUK SSSR -- SERIYA KHIMICHESKAYA in Russian
No 11, Nov 77 p 2637 manuscript received 12 Sep 77

PUDOVIK, M. A., KIBARDINA, L. K., PESTOVA, T. A. and PUDOVIK, A. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov and Kazan Branch of the Academy of Sciences USSR

[Abstract] The reaction of acid chlorides of trivalent phosphorus with N-trimethylsilylamines leads to the formation of N-alkyl(aryl)aminophosphines. In contrast, the reaction of these acid chlorides with N-trimethylsilylacetamides results in the formation of cyclic phosphites:



R = CH₂CH(CH₃) (I); (CH₂)₃ (II); CH₂CH₂CH(CH₃) (III); o-C₆H₄ (IV)

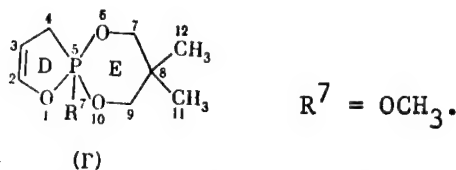
The product yield ranges from 55-90%. Structural identification of the resulting acids was made on the basis of published data and IR and H¹ and p³¹ NMR spectroscopy. The first step in the reaction is the elimination of HCl. The N-trimethylsilylamidophosphites which are formed during heating decompose with the elimination of acetonitrile into the corresponding silylphosphites which by the addition of HCl via the Arbuzov reaction react to form the acid phosphates. References 4: 2 Russian, 2 Western.

STEREOCHEMISTRY OF ORGANOPHOSPHORUS COMPOUNDS. REPORT 15. SYNTHESIS AND
EASE OF REARRANGEMENT OF 1,6,10-TRIOXY-8,8-DIMETHYL[(5-METHOXY)-5-PHOPHASPIRO-
(4,5)] Decene-2

Moscow IZVESTIYA AKADEMII NAUK SSSR -- SERIYA KHIMICHESKAYA in Russian No 9,
Sep 77 pp 2000-2006 manuscript received 20 Jul 76

ARBUZOV, B. A., SAMITOV, YU. YU., MAREYEV, YU. M., VINOGRADOVA, V. S.,
Chemical Institute imeni A. M. Butlerova and Kazan State University imeni
V. I. Ul'yanova-Lenina

[Abstract] A study was made of the dynamic stereochemistry of the title
compound, which has the structure shown below, from the point of view of
its tendency towards pseudorotation.



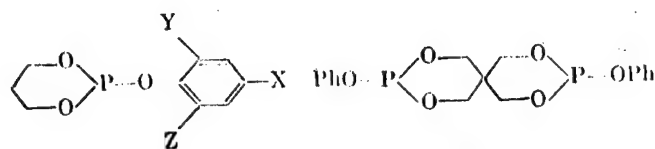
This compound was prepared by reaction of acrolein with 5,5-dimethyl-2-methoxy-1,3,2-dioxaphosphorinane. The structure of the product was confirmed chemically and by NMR- H^1 and P, 31 and IR spectroscopy. An NMR examination of the title compound in the temperature range -50° to $80^\circ C$ in order to establish the rotational changes was carried out. With increasing temperature, beginning at 32° the singlet line becomes a doublet and the amplitude of the higher field line becomes less than the lower field line. This indicates the presence of unresolved spin-spin multiplicity for the high field line, apparently caused by some long-range interaction with a small $4J_{HH}$, constant. Other features of the spectra, such as the gem-dimethyl group at C⁸ are also considered. References 10: 6 Russian, 4 Western.

THREE-DIMENSIONAL STRUCTURE OF PHOSPHORUS-CONTAINING HETEROCYCLIC COMPOUNDS.
REPORT 18. 2-PHENOXY-1,3,2-DIOXYPHOSPHINANES

Moscow IZVESTIYA AKADEMII NAUK SSSR -- SERIYA KHIMICHESKAYA in Russian No 9,
Sep 77 pp 2006-2011 manuscript received 7 Jul 76

ARBUZOV, B. A., ARSHENOVA, R. P., SOROKIN, T. D., REMIZOV, A. B., and KOROLEVA,
G. YE., Chemical Institute imeni A. M. Butlerova and Kazan State University
imeni V. I. Ul'yanova-Lenina

[Abstract] The compounds examined in this study, having the following
structures, in contrast to those previously studied by similar methods, contain
P atoms with an



(I), (III)–(VII)

(II)

X = Y = Z = H (I); X = Br, Y = Z = H (III); X = NO₂, Y = Z = H (IV);
 X = Y = Z = *t*-Bu (V); X = Z = H, Y = Br (VI); X = Z = H, Y = NO₂ (VII)

unsymmetrical environment, so that the two cyclic P-O bonds occur in the vicinity of alkyl groups, while the exocyclic P-O bonds is associated with a benzene ring. IR spectra were run on both crystals and solutions of these compounds to determine the various rotational conformations and the P-O bond characteristics, so as the dipole moment and polarizability are elipsoidal. The phenoxy group is shown to have a cis-axial orientation. The plane of the benzene ring is perpendicular to the plane of the P-O-C bonds.
 References 12: 9 Russian, 3 Western.

USSR

UDC 547.913.5

SYNTHESIS OF MOLECULES OF THE TRIESTER PHOSPHATIDYL- AND THIOPHOSPHATIDYL (P→O) SERINES

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 8, No 7, Jul 77 pp 1392-1397 manuscript received 15 Jul 76

PREDVODITELEV, D. A., KVANTRISHVILI, V. B., and NIFANT'YEV, E. YE., Moscow State Pedagogical Institute imeni V. I. Lenin

[Abstract] Two methods of synthesis have been reported for models of novel types of triester phosphatidyl- and thiophosphatidyl-(P→O)-serines. The first involved sulfohydrolysis of 3-diethylamido-(2-carbethoxy-2-tritylaminoethyl)-phosphite-1,2-isopropylidene glycerine to the thio-phosphite, which without any purification was subjected to Todd-Atterton reaction. The second method was based on the addition of sulfur to nonsymmetric phosphites and amidophosphites containing isopropylidene glycerine and serine fractions. Figure 1; references 7: 5 Russian, 2 Western.

USSR

UDC 542.91:547.1'118

SYNTHESIS OF SOME ORGANOPHOSPHORUS AGENTS CAPABLE OF SOLVATING CATIONS AND SOLVENTS

Moscow IZVESTIYA AKADEMII NAUK--SERIYA KHIMICHESKAYA in Russian No 7, Jul 77
pp 1578-1581 manuscript received 5 Mar 76

OSIPENKO, N. G., TSVETKOV, YE. N., SHCHERBINA, T. M., RANNEVA, YU. I.,
PETROV, E. S., SHATENSHTYEN, A. I., and KABACHNIK, M. I., Institute of
Organometallic Compounds Academy of Sciences USSR and Physical-Chemical
Institute imeni L. Ya. Karpov

[Abstract] In an attempt to clarify the structural effect of phosphine oxides on their solvating properties, a series of phosphine oxides has been synthesized by the Michaelis-Becker reaction which contains fragments of simple esters, amines and aminoesters. Several analogues of methyldi-(methoxymethyl)-phosphine oxide containing complex ester fragments as well as analogues of hexamethylthiamidophosphate were also synthesized. Table 1; references 17: 12 Russian, 5 Western.

USSR

UDC 541.63:541.49:547.1'118

ACID-BASE PROPERTIES OF PHOSPHORUS COMPOUNDS. COMMUNICATION 12. STEREO-CHEMISTRY OF THE COMPLEXES WITH AN H-BOND OF THE PHOSPHORYL COMPOUNDS

Moscow IZVESTIYA AKADEMII NAUK--SERIYA KHIMICHESKAYA in Russian No 7, Jul 77
pp 1531-1534 manuscript received 19 Apr 76

MATROSOV, YE. I., PETROV, G. M., and KABACHNIK, M. I., Institute of Organometallic Compounds, Academy of Sciences USSR

[Abstract] On the basis of dipole moment determinations based on the $R_3P=O...HOR'$ type complexes with weak H-bonds ($\Delta\mu_H 0$), it has been established that the coordination angle of the phosphoryl group in the H-bond is $109 \pm 6^\circ$. This led the authors to the conclusion that the complexes of phosphoryl compounds exhibit free rotation around the H-bond. Table 1, figures 2, references 13: 8 Russian, 5 Western.

USSR

UDC 541.67

KERR EFFECT AND THE STRUCTURES OF ORGANOPHOSPHORIC COMPOUNDS

Moscow USPEKHI KHIMII in Russian Vol 46, No 9, Sep 77 pp 1544-1577

ARSHINOVA, R. P., Scientific Research Chemical Institute imeni A. M. Butlerov, Kazan' State University imeni V. I. Ul'yanov-Lenin

[Abstract] Polarity and polarizability are basic properties of any substance which determine its structure and reactivity. These characteristics can be studied only by a few experimental methods, the most important being the determination of the dipole moments and the Kerr effect. This article reviews the experimental work on the spacial and electronic structures of organophosphorus compounds. Additive values of the refractions, polarities and polarizabilities of phosphorus bonds have been analyzed. Data on conformational analysis of the acyclic and of the 4-, 5- and 6-membered phosphorus containing heterocycles have been compiled; reports were made on the internal rotations in acyclic compounds and on the effect of conjugation. Determination of Kerr constants and light dispersion gives a unique method for the investigation of the deviation of phenyl ring from planarity. The review also covers spacial and electronic effects of trivalent phosphorus compounds. Experimental values of Kerr constants, phosphorus bond refractions for the D line Na^{35} , the dipole moments, and bond polarizability have been tabulated. Figures 13; references 130: 86 Russian, 44 Western.

USSR

UDC 547.241

PROBLEMS CONCERNING THE STRUCTURE AND REACTIVITY OF TRICOORDINATED PHOSPHORUS THIOACID ESTERS

Moscow USPEKHI KHIMII in Russian Vol 46, No 9, Sep 77 pp 1638-1657

KRASIL'NIKOVA, YE. A., Kazan' Chemical-Technological Institute imeni S. M. Kirov

[Abstract] Although the chemistry of tricoordinated phosphorus has been studied quite thoroughly, the reports concerning the structure and reactivity of the tricoordinated phosphorus compounds with a P-S bond are rather meager. The esters of tricoordinated phosphorus thioacids have two nucleophilic reaction centers: phosphorus and sulfur. The review covers characteristic reactions of such compounds with electrophilic reagents. It has been concluded that the reactions of phosphoric thioacid esters $\text{R}_n\text{P}(\text{SR}')_{3-n}$ with electrophilic reagents are affected by the presence of two competing nucleophilic centers, by dual reactivity of the phosphorus (III)-sulfur (II) group, and by high reactivity of dicoordinated thio- and thione-sulfur atom in the esters of tri- and tetracoordinated phosphorus compounds. Figures 2; references 170: 99 Russian, 71 Western.

USSR

UDC 547.558.1

CHEMISTRY OF DIHYDROPHENOPHOSPHAZINES

Moscow USPEKHI KHIMII in Russian Vol 46, No 9, Sep 77 pp 1625-1637

BOKANOV, A. I. and STEPANOV, B. I., Moscow Chemical-Technological Institute
imeni D. I. Mendeleev

[Abstract] A review of 40 references covers the synthesis of 5,10-dihydrophenophosphazines and their properties. Most of the available knowledge on these compounds was gained within the last two decades, although the first reference dates back to 1890. The 5,10-dihydrophenophosphazines are phosphoric analogues of phenothiazines and they are used as antioxidants and as therapeutic agents. The review consists of three parts: synthetic methods, reactions of the title compounds, and physical-chemical properties. References 40: 16 Russian, 24 Western.

USSR

UDC 546.18

PHOSPHONITRIDES

Moscow USPEKHI KHIMII in Russian Vol 46, No 9, Sep 77 pp 1604-1624

BORISOV, YE. V. and NIFANT'YEV, E. YE., Moscow State Pedagogical Institute
imeni V. I. Lenin

[Abstract] Although more than 100 years have passed since the first synthesis of phosphonitrides, the reviews which appeared so far have not covered adequately the questions of their structures, properties and reactivity. This particular review covers all of the literature references up to January 1976. The first three chapters, covering the synthesis, physical properties and electronic structure, are organized by structural entities: PN compounds followed by polyhydroxyphosphonitrides (NPO) as well as their thio analogues (NPS). Separate chapters are devoted to the electrophysical properties, the practical application of these compounds, and to industrial synthesis of phosphonitrides. Figure 1; references 169: 47 Russian, 1 Polish, 1 Hungarian, 120 Western.

USSR

UDC 547.26'118:541.127:542.938

KINETICS OF THE HYDROLYSIS OF PHOSPHORIC ACID ESTERS

Moscow USPEKHI KHIMII in Russian Vol 46, No 9, Sep 77 pp 1578-1603

BEL'SKIY, V. YE., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan' Branch of the Academy of Sciences USSR

[Abstract] Hydrolysis of phosphoric acid esters was studied intensively which led to a wide utilization of these agents in technology, agriculture and medicine. The reactivity of phosphoric acid ester bonds ranges through several orders of magnitude and there often exists the need for an a priori estimation of these values which is mostly done empirically by assuming a linear relationship of the free energy in various chemical processes. The review is devoted to the kinetics of the hydrolysis of phosphoric acid esters in acid, base and neutral media, analyzing the mechanisms of the hydrolysis of various mono-, di- and triesters. Literature references concerning a number of parameters have been compiled in tables and graphs. The author acknowledges a rather limited number of the compounds considered -- 140 out of virtually thousands of various mono-, di- and triphosphates -- urging further studies in this area. Figures 9; references 106: 11 Russian, 1 Czech, 94 Western.

USSR

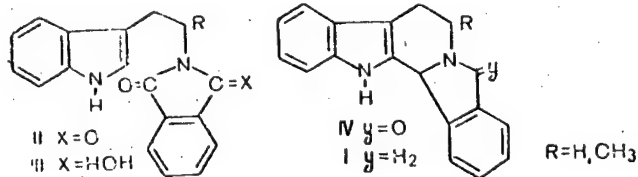
UDC 521.124+661.185.233+547.313.2

ALKALINE CLEAVAGE OF TRIPHENYL- AND TRIBUTYLPHOSPHONIUM SALTS THAT CONTAIN THE α -ALKOXYVINYL GROUP

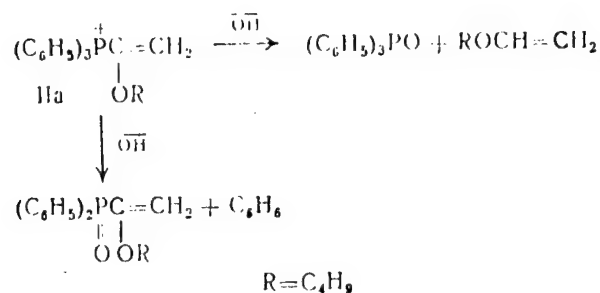
Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian Vol 30, No 7, 1977 pp 596-599 manuscript received 12 Apr 77

TORGOMYAN, A. M., KHACHATRYAN, R. A., OVAKIMYAN, M. ZH. and INDZHIKYAN, M. G., Institute of Organic Chemistry of the Academy of Sciences ArmSSR

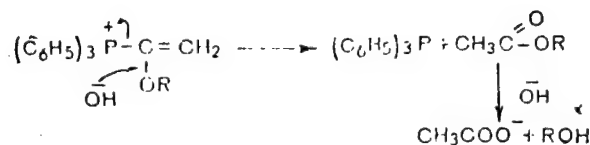
[Abstract] Previous research by the authors showed that triphenylphosphonium salts I with the α -alkoxy- β -bromoethyl group react with alkali hydroxide to form benzene and alkyl vinyl ether. In this paper the research is continued with an investigation of alkali hydroxide cleavage of alkoxyvinylphosphonium salts II, which are the dehydrobrominated analogs of salts I.



Reacting salt IIa with caustic potash gives nonphosphoric reaction products of butyl vinyl ether, acetic acid and small amounts of benzene, and phosphoric products of triphenylphosphorus and triphenylphosphorus oxide. Butyl vinyl ether and benzene are the result of two competitive reactions of paraffin cleavage involving the phenyl and alkoxyvinyl groups.



The acetic acid is formed by nucleophilic substitution at the α -alkoxyvinyl group of the phosphonium complex.



An analogous pattern was observed in the case of salt IIb. The results show incomparably greater anionic mobility of the alkoxyvinyl group than the phenyl group. References 2: 1 Russian, 1 Western.

USSR

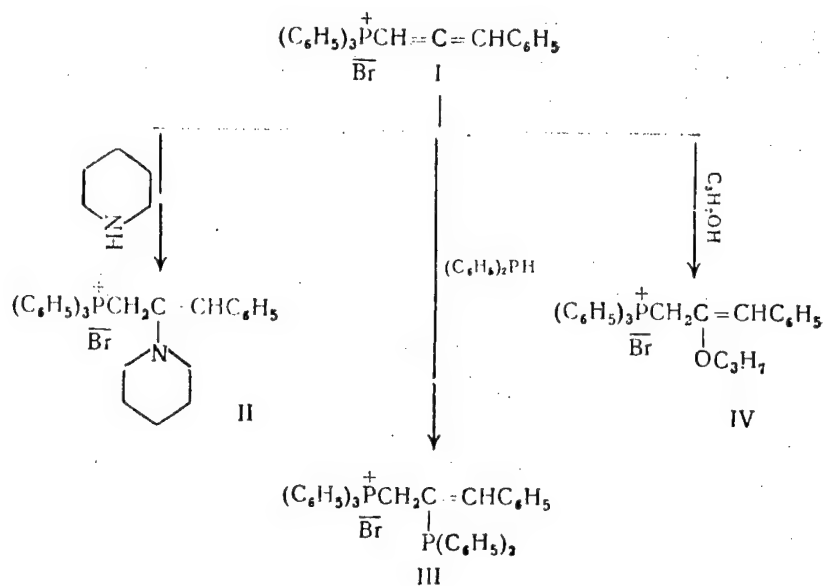
UDC 546.18+547.315.1

NUCLEOPHILIC ADDITION TO A TRIPHENYL(3-PHENYL-1,2-PROPADIENYL)PHOSPHONIUM SALT

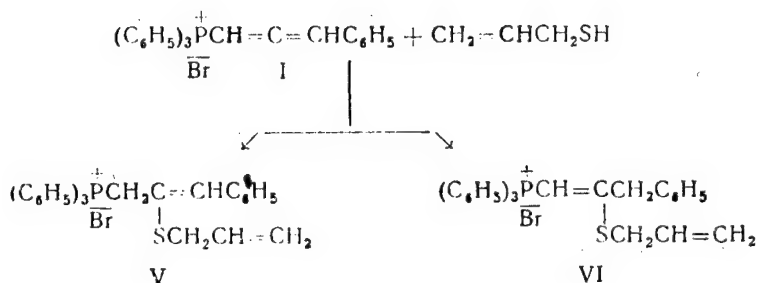
Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian Vol 30, No 7, 1977 pp 582-587
manuscript received 12 Apr 77

AKLYAN, ZH. A., KHACHATRYAN, R. A., KINOYAN, F. S. and INDZHIKYAN, M. G.,
Institute of Organic Chemistry, Academy of Sciences ArmSSR

[Abstract] The authors recently described reactions of diethylamine and butyl alcohol with triphenyl(3-phenyl-1,2-propadienyl)phosphonium bromide (I). This article, which is a continuation of the previous research, is devoted to the reaction of salt I with piperidine, propyl alcohol, allyl- and butylmercaptans, diphenyl phosphine and triethyl phosphite. Piperidine and diphenyl phosphine react readily with I at room temperature, to form individual inclusion products involving the α,β -unsaturated bond. The reaction with propyl alcohol is similar, but takes place at 70°C.



Mercaptans undergo addition to allenylphosphonium salt I with much more difficulty. Heating on a boiling water bath is necessary for adding butylmercaptan. Completion of the addition of allylmercaptan requires heating at 140°C for 2 hours. In the former case an addition product is formed that involves the α,β -unsaturated bond, while in the latter case a mixture of adducts is formed involving both unsaturated groups of the phosphonium complex.



It is shown that the α,β -isomer is obtained as a result of prototropic isomerization of the β,γ -isomer under the conditions of the reaction.
Reference 1: Russian.

USSR

UDC 547.24

REACTION OF DIALKYLAMINODICHLOROPHOSPHINES WITH ALKALI METAL IODIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian No 8, Aug 77 pp 1916-1917
manuscript received 15 Nov 76

GORBATENKO, ZH. K. and FESHCHENKO, N. G., Institute of Organic Chemistry,
Academy of Sciences, Ukrainian SSR

[Abstract] Repetition of an earlier work involving the interaction of dialkylaminodichlorophosphines with lithium iodide in a boiling benzene solution reveals that the reaction of the dialkylaminodichlorophosphines with lithium iodide (or sodium or potassium iodide) results in the formation of only dialkylaminodiiodophosphines, regardless of the reaction conditions. Long-term boiling of the reaction mixture in a benzene solution or illumination of the dialkylaminodiiodophosphine results in its partial or complete decomposition to form phosphorus diiodide and compounds of the composition $\text{Alk}_4\text{I}_4\text{N}_2$. References: 2 Russian.

USSR

UDC 547.241

DIALKYLAMINODIIODOPHOSPHINES, BIS(DIALKYLAMINO)IODOPHOSPHINES AND
TRIS(DIALKYLAMINO)IODOPHOSPHONIUM TRIIODIDE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian No 8, Aug 77 pp 1915-1916
manuscript received 15 Nov 76

GORBATENKO, ZH. K. and FESHCHENKO, N. G., Institute of Organic Chemistry,
Academy of Sciences, Ukrainian SSR

[Abstract] It was established that the reaction of PI_3 with morpholino-trimethylsilane is a general reaction, and that any dialkylaminotrimethylsilane interacts with PI_3 to form dialkylaminodiiodophosphines. The properties of these compounds are described. The iodine atom in bis(dialkylamino)iodophosphines cannot be substituted, even by an excess of dialkylaminotrimethylsilane, although when dialkylamines act on these compounds, the iodine atom is easily replaced by a dialkylamino group. References: 2 Russian.

USSR

UDC 547.241+547.785.3

BENZIMIDAZOLYL ALKYL ESTERS OF METHYLPHOSPHONIC ACID AND THEIR PROPERTIES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian No 8, Aug 77 p 1915 manuscript received 10 Nov 76

SHISHKIN, V. YE., YUKHNO, YU. M. and NO, B. I., Volgograd Polytechnical Institute

[Abstract] The condensation of equimolar quantities of the hydrochlorides of esters of alkyl- ω -imino- ω -alkoxyalkylmethylphosphonates with orthophenylinediamine in alcohol was used to produce alkyl-2-benzimidizolylalkylmethylphosphonates. The reaction lasts for 2.5-3 hours, the temperature mode being limited by the temperature of decomposition of the salts of phosphorylated imino esters. References: 2 Russian.

USSR

UDC 547.26'118

THE REACTION OF TRIETHYLPHOSPHITE WITH p-BENZOQUINONE IN THE PRESENCE OF HYDROGEN CHLORIDE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian No 8, Aug 77 p 1914 manuscript received 4 Dec 76

GAZIZOV, T. KH., KIBARDIN, A. M., and PUDOVNIK, A. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan' Affiliate, Academy of Sciences, USSR

[Abstract] Trialkyl phosphites interact with p-benzoquinone to form dialkyl p-alkoxyphenylphosphates. It is assumed that these reactions begin by an attack of the phosphorus atom of the phosphite on the carbonyl oxygen of the quinone. Reactions of triethyl phosphite with benzoquinone in the presence of hydrogen chloride in ether at -70 C lead to the formation of a mixture of phosphate and phosphonate. The quantitative composition of the reaction product after film distillation corresponds to 1:1 attachments. The reaction may begin with an attack of the phosphorus atom on the carbonyl oxygen (I), the carbon (II) or the activated carbon-carbon bond (III). The results produced indicate that triethylphosphite interacts with p-benzoquinone in the presence of HCl in a reaction which begins at least partially with attack of the phosphorus atom on the carbon atom of the activated carbon-carbon double bond. References: 2 Russian.

USSR

UDC 546.183+547.446

ACID ALKYL(ALKENE-1-YL)PHOSPHITES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian No 8, Aug 77 pp 1913 manuscript received 17 Nov 76

IVANOVA, ZH. M., KIM, T. V., and GOLOLOBOV, YU. G., Institute of Organic Chemistry Academy of Sciences Ukrainian SSR

[Abstract] Acid phosphites containing an α -alkenyl ester group have been synthesized for the first time by the interaction of alkyl dichlorophosphites with 2-chlorocyclohexanone and triethylamine, forming alkyl(2-chlorocyclohexen-1-yl)chlorophosphites, which, upon hydrolysis with a calculated quantity of water mixed with ether and acetone at -30 C in the presence of triethylamine are converted to alkyl(2-chlorocyclohexen-1-yl)-phosphites. References: 2 Russian.

USSR

UDC 547.26'118

INTERACTION OF ORGANOPHOSPHORUS DISULFIDES WITH ORGANIC COMPOUNDS OF MAGNESIUM

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian No 8, Aug 77 pp 1912-1913 manuscript received 14 Oct 76

KHASKIN, B. A., RYMAREVA, T. G., and MEL'NIKOV, N. N., All-Union Scientific Research Institute for Chemical Means of Plant Protection

[Abstract] The authors showed previously that phosphorus-containing disulfides react with sodium derivatives of β - and γ -dicarbonyl compounds to form the corresponding esters and salts of phosphorus dithioacids. However, when equimolar quantities of disulfides and magnesium aniline halides interact in absolute diethyl ether at 30-34 C, the corresponding triphosphorylsulphenamides cannot be produced, but rather free sulfur is liberated and anilides and salts of dithiophosphoric acids are produced. References 4: 1 Russian, 3 Western.

USSR

UDC 546.18+547.421.51.262

SYNTHESIS OF FUNCTIONALLY SUBSTITUTED ALKYL DICHLOROPHOSPHITES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian No 8, Aug 77 p 1912 manuscript received 30 Nov 76

GAZIZOV, M. B., TSIVUNIN, V. S., OSTANINA, L. P. and SHAYKHUTDINOVA, F. I.,
Kazan' Institute of Chemical Technology imeni S. M. Kirov

[Abstract] Certain functionally substituted alkyl dichlorophosphites cannot be produced by the ordinary method of synthesis. The authors synthesized these compounds containing such important functional groups as nitro and ester groups by interacting asymmetrical acetals with PCl_3 in a ratio of 1:2 with cooling.

USSR

UDC 547.341

INTERACTION OF ENOLPHOSPHATES WITH PHOSPHORUS PENTACHLORIDE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian No 8, Aug 77 p 1911 manuscript received 6 Dec 76

ROZINOV, V. G., KOLBINA, V. YE., GLUKHIKH, V. I. and KLIMOV, YU. A.

[Abstract] It is established that when a solution of phosphorus pentachloride in benzene acts upon enol phosphates insoluble complexes are produced, from which, by acetic acid treatment, dichlorides of substituted vinylphosphonic acids can be obtained (II). Apparently, the phosphorus pentachloride causes the formation of enoldichlorophosphate from I which, upon further interaction with the phosphorus pentachloride, either decomposes to form a substituted acetylene or is converted to enolphosphoran which decomposes to form acetylene, which is phosphorylated by the phosphorus pentachloride. References: 2 Russian.

USSR

UDC 541.438.1

THE INTERACTION OF SECONDARY PHOSPHINES WITH QUINONES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian No 8, Aug 77 p 1910 manuscript received 6 Dec 76

PUDOVIK, A. N., ROMANOV, G. V. and POZHIDAYEV, V. M., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan' Affiliate, Academy of Sciences, USSR

[Abstract] It was found that when secondary phosphines interact with p-quinones, p-oxyarylphosphine oxides and aryl esters of phosphinic acids are formed. A decrease in the reaction temperature and an increase in the quantity of solvent tend to increase the yield of the p-oxyarylphosphine oxides.

USSR

UDC 547.25.118.07

SOME PHYSICAL AND CHEMICAL PROPERTIES OF THE HYDROCHLORIDES OF ARYL ESTERS OF HYDRAZIDO-N, N-DI(2-CHLOROETHYL)AMIDOPHOSPHORIC ACIDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian No 8, Aug 77 pp 1737-1740 manuscript received 23 Oct 75

OVROUTSKIY, V. M., PROTSENKO, L. D., SACHENKO, L. G. and DENISOV, N. D.

[Abstract] In order to establish the relationship between structure and properties, the ionization constants were measured and polarographic behavior studied of hydrochlorides of aryl esters of hydrazido-N, N-di(2-chloroethyl)-amidophosphoric acid. The ionization constants were found to be linearly dependent on the constants σ^0 and σ^* of Hammett and Taft. Linear variation of the half-wave potentials with ionization constants of the salts and the σ^* constants was established. References 9: 6 Russian, 3 Western.

USSR

UDC 546.185:543.51

MASS SPECTRA OF (1,1,3-TRIHYDROTETRAFLUOROPROPOXY)CHLOROCYCLOTRIPHOSPHAZENES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian No 8, Aug 77 pp 1732-1736
manuscript received 12 Jan 76

FEDOROV, S. G., KARPENKO, N. F., GOL'DIN, G. S., ZAPUSKALOVA, S. F. and
CHIZHOV, O. S.

[Abstract] The behavior of a series of tetrafluoropropoxychlorocyclotri-phosphazenes is described, with the substituents located nongeminally in the case of disubstituted and trisubstituted cyclophosphzenes, while in the case of tetrasubstituted cyclophosphazenes there is only one pair of gem substituents. The characteristic features of fragmentation under electron impact of a number of fluoroalkoxychlorocyclophosphazenes are found. Basically, ions containing a 6-membered ring are formed. Rearrangements also occur. References 6 : 1 Russian, 5 Western.

USSR

UDC 547.241+541.124

KINETICS OF PHENOLYSIS OF ACID AMIDES OF TRIVALENT PHOSPHORUS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian No 8, Aug 77 pp 1726-1732
manuscript received 12 Jan 76

YEVADKOV, V. P., BEKETOV, V. P. and BRYANTSEV, B. I.

[Abstract] A study was made of the kinetics of phenolysis of a number of amodophosphites and the influence of the nature of the solvent and acidic and basic substances on the reaction rate. Phenolysis of trivalent phosphorus acid amides is a second order reaction. The reaction rate in the compounds studied increases with increasing basicity of the nitrogen atom and electrophilicity of the phosphorus atom in the amide, and also with increasing acidity of the phenol. Phenolysis is inhibited in the presence of bases. References 21: 11 Russian, 10 Western.

USSR

UDC 547.241+542.91+541.49

SYNTHESIS AND COMPLEX-FORMING PROPERTIES OF AMINOMETHYLENEBISPHOSPHONIC ACID

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian No 8, Aug 77 pp 1721-1726
manuscript received 2 Feb 76

RUSINA, M. N., BALASHOVA, T. M., ZHADANOV, B. V., TSITRINA, A. YU., and
POLYAKOVA, I. A., All-Union Scientific Research Institute for Chemical
Reagents and Highly Pure Substances

[Abstract] The purpose of the work was the production of the simplest representative of the class of aminoalkylidenebisphosphonic acid - amino-methylenebisphosphonic acid and the study of its acidic and complex-forming properties. The combination in the molecule of geminal phosphonic groups and amino groups leads to the formation of complexes with metals of various compositions and solubilities. It is established that aminomethylenebisphosphonic acid combines with alkali earth and transition metals to form insoluble complexes of the composition MeH_2L , $\text{Me}_3(\text{HL})_2$ and Me_2L and the soluble complex MeL . References 6: 4 Russian, 2 Western.

USSR

UDC 547.558:495

SALTS AND ILIDES OF PHOSPHONIUM BASED ON CHLOROACETYLUREA

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian No 8, Aug 77 pp 1715-1721
manuscript received 19 Jan 76

KUSHNIR, V. N., SHEVCHUK, M. I. and DOMBROVSKIY, A. V., Chernovitsa State University

[Abstract] Chloroacetylurea forms a crystalline phosphonium salt when heated in dioxane with triphenylphosphonium in practically quantitative yield. When this salt interacts with a solution of ammonia, a crystalline, highly reactive phosphonium ilide is formed. At room temperature when the ilid is heated, it reacts with bromine, iodine bromide, methyl iodide and trimethylchlorosilane to yield α -substituted phosphonium salts. Phosphonium halides are easily dehydrohalogenated by soda in water and methanol to yield crystalline urea-carbobromomethylene-, ureacarboiodomethylene- and ureaethylidenetriphenylphosphonium ilids. The new ilid undergoes the Wittig reaction with aromatic and heterocyclic aldehydes more actively than the β -oxophosphoranes described earlier. This produces N-cinnamoyl- and N-(β -substituted)acryloyl derivatives of urea containing aryl, heterocyclic and condensed aromatic rings, conjugated with ethylene and peptide bonds. A table of the compounds produced is presented. References 4: 3 Russian, 1 Western.

REACTION OF ISOCYANATES AND ISOTHIOCYANATES OF THIOPHOSPHORIC ACID AMIDO ESTERS WITH NUCLEOPHILIC REAGENTS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian No 8, Aug 77 pp 1711-1715
manuscript received 26 Jan 76

MEL'NIKOV, N. N., KRYLOVA, T. P., and VLADIMIROVA, I. L., All-Union Scientific Research Institute for Chemical Means of Plant Protection

[Abstract] A method was developed for the synthesis of isocyanates and isothiocyanates. Isocyanates of N, N-dialkylamido esters of thiophosphoric acid were produced by the action of carbonyl chloride on O-alkyl-N, N-dialkylamidothiophosphoric acid amides in carbon tetrachloride. Isothiocyanates of O-alkyl-N, N-dialkylamidothiophosphoric acid were produced by the reaction of O-alkyl-N, N-dialkylamidochlorothiophosphates with potassium thiocyanate in the presence of catalytic quantities of pyridine. References 3: all Russian.

SOME REACTIONS OF THE DIHYDRAZIDES OF PHOSPHORUS THIOACIDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian No 8, Aug 77 pp 1704-1711
manuscript received 31 Dec 75

GRAPOV, A. F., MIKHAYLOVA, O. B., and MEL'NIKOV, N. N.

[Abstract] The reactions of the dihydrazides of phosphorus thioacids with carbonyl compounds such as aldehydes, ketones, α - and β -diketones, glyoxal, benzoyl chloride, isocyanates and isothiocyanates were studied. When dihydrazidomethylphosphonate reacts with aldehydes and ketones, the corresponding hydrazones are formed. Aldazines and ketazines are formed as side products. When the dihydrazides are reacted with α -diketones, 3-thio-3,1,2,4,5-phosphatetetraazacyclohepta-5, 7-dienes or di(α -acetylalkylidene-[or benzylidene]hydrazido)thiophosphonates (or thiophosphates) are formed, depending on the ratio of the components. The dihydrazides of thiophosphonic and thiophosphoric acids react with β -diketones and acetoacetic ester, yielding 3,5-disubstituted pyrazoles or 3-substituted pyrazolones. Acylation of dihydrazidomethylthiophosphonate with benzoyl chloride forms 3-phospho-7-oxa-1,2,4,5-tetraazacyclooxa-5,8-diene. References 23: 8 Russian, 15 Western.

USSR

UDC 547.26'118

AMINOPHOSPHONATE-AMIDOPHOSPHATE REGROUPING IN THE REACTIONS OF DIALKYL-
PHOSPHITES WITH BENZALANILINE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian No 8, Aug 77 pp 1698-1703
manuscript received 30 Mar 76

PUDOVIK, A. N., KONOVALOVA, I. V., ZIMIN, M. G., DVOYNISHNIKOVA, T. A.,
VINOGRADOV, L. I. and SAMITOV, YU. YU., Kazan' State University

[Abstract] A study was made of the reaction of diethyl-, dipropyl- and diisopropylphosphorous acids benzalaniline and the regrouping of the aminophosphonic acid esters thus formed. The interaction of dialkyl phosphites with benzalaniline in the presence of catalytic quantities of bases leads to the formation of dialkyl esters of N-phenylaminobenzylphosphonic acids, while in the presence of equimolar quantities of sodium, potassium or magnesium salts, the dialkyl phosphites are accompanied by aminophosphonate-amidophosphonate rearrangement with the formation of dialkyl esters of N-phenyl-N-benzylamidophosphoric acids. NMR spectroscopy was used to establish the primary conformation of the diethyl ester of N-phenylaminobenzylphosphonic acid. References 14: 10 Russian, 4 Western.

USSR

UDC 547.26'118

THE INTERACTION OF DIETHYLPHOSPHOROUS ACID WITH SUBSTITUTED BENZALANILINES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian No 8, Aug 77 pp 1694-1698
manuscript received 17 Oct 75

PUDOVIK, A. N., KONOVALOVA, I. V., ZIMIN, M. G., DVOYNISHNIKOVA, T. A., and
POZHIDAYEV, V. M., Kazan' State University

[Abstract] In order to continue their study of the regularities of aminophosphonate-amidophosphonate regrouping, the authors studied the reaction of diethylphosphorous acid with N-substituted benzalaniline and the stability of the α -aminophosphonates thus formed. When the reaction was conducted in the presence of catalytic quantities of sodium ethylate or diethylphosphide, diethyl esters of N-phenol substituted aminobenzylphosphonic acids were formed. When the diethyl esters were heated to 190-210°C, they decomposed to the initial compounds, a process which was accelerated in the presence of butyllithium. When the first reaction was conducted in the presence of equimolar quantities of sodium diethylphosphide, diethyl esters of N-phenyl substituted N-benzylamidophosphoric acid were formed. References 5: 4 Russian, 1 Western.

USSR

UDC 542.91:547.379.2+547.26'118

THE NONCLASSICAL ARBUZOV REGROUPING. REACTION OF ALKYLPHENYLSULPHONIUM ILIDES OF DIMEDONE WITH TRIALKYLPHOSPHITES

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 236, No 2, 1977 pp 358-359
manuscript received 3 May 77

BELKIN, YU. V., POLEZHAYEVA, N. A. and ARBUZOV, B. A., A. M. Butlerov Scientific Research Institute for Chemistry; Kazan' State University

[Abstract] The authors established earlier that triphenylphosphine and tris-(dimethylamino)-phosphine dialkylate carbonyl-stabilized ilides of sulphonium react to form phosphonium salts. A study of the reactions of 2-methylphenylsulfuranylidene dimedone (Ia) with triethyl phosphite (TEP) and 2-benzylphenylsulfuranylidene dimedone (Ib) with trimethyl phosphite (TMP) showed that ethyl (IVa) and methyl (IVb) esters of 2-phenylsulphenyl dimedone, diethylmethylphosphonate (VIa), dimethylmethylphosphonate (VIb), triethyl (VIIa) and trimethyl (VIIb) phosphates are formed. Obviously, the trialkyl phosphites dealkylate Ia, and Ib to form a quasi-phosphonium salt according to the first stage of the Arbuzov rearrangement. Thus, the reaction of carbonyl-stabilized ilids of sulphonium with trialkyl phosphites represent a new nonclassical rearrangement. The quasi-phosphonium salt formed in the first stage of the rearrangement can be dealkylated either by an enolate ion or by a molecule of the initial phosphite. References 4: all Russian.

USSR

UDC 541.64:547.241

KINETICS OF MECHANISMS OF RADICAL POLYMERIZATION OF DIALKYLVINYLPHOSPHONATES

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 236, No 2, 1977 pp 387-389
manuscript received 8 May 77

LEVIN, YA. A., BRIUS, A. A., and IVANOV, B. YE., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov; Kazan' Affiliate of Academy of Sciences, USSR

[Abstract] Free-radical polymerization of vinyl derivatives of tetra-coordinated phosphorus differs significantly from polymerization of structurally similar organic monomers with a carbonyl group in place of the phosphoryl, and also from polymerization of organophosphorus monomers with the vinyl group remote from the phosphorus atom. Up to this time, only a few aspects of the gross kinetics of radical polymerization of these monomers have been studied. The kinetics of polymerization was studied in this article by a refractometric method using di-ter-butylperoxide as the photosensitive initiator. Processing of the results by regression analysis produced a 95% level of reliability. Radical polymerization of vinyl phosphonates shows a sharp departure from the

smooth dependence of the chain growth rate constant, activation energy, and A_p on the Q factor characterizing the resonant stabilization of the monomer and from the polymerization enthalpy ΔH , so that during growth and rupture of kinetic chains accompanying radical polymerization of vinylphosphonates, factors are at work which are absent during polymerization of purely organic monomers. References 15: 11 Russian, 4 Western.

USSR

UDC 543.253

POLAROGRAPHIC INVESTIGATION OF MIXED LIGAND COMPLEX COMPOUNDS OF PALLADIUM (II) AND PLATINUM (II) THAT CONTAIN TRIALKYL PHOSPHITES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 47, No 9, Sep 77 pp 2033-2037
manuscript received 2 Aug 76

BUDNIKOV, G. K., ULAKHOVICH, N. A., ORLOVA, I. A., TROITSKAYA, A. D. and KOSHURNIKOVA, I. V., Kazan' State University, Kazan' Institute of Chemical Technology

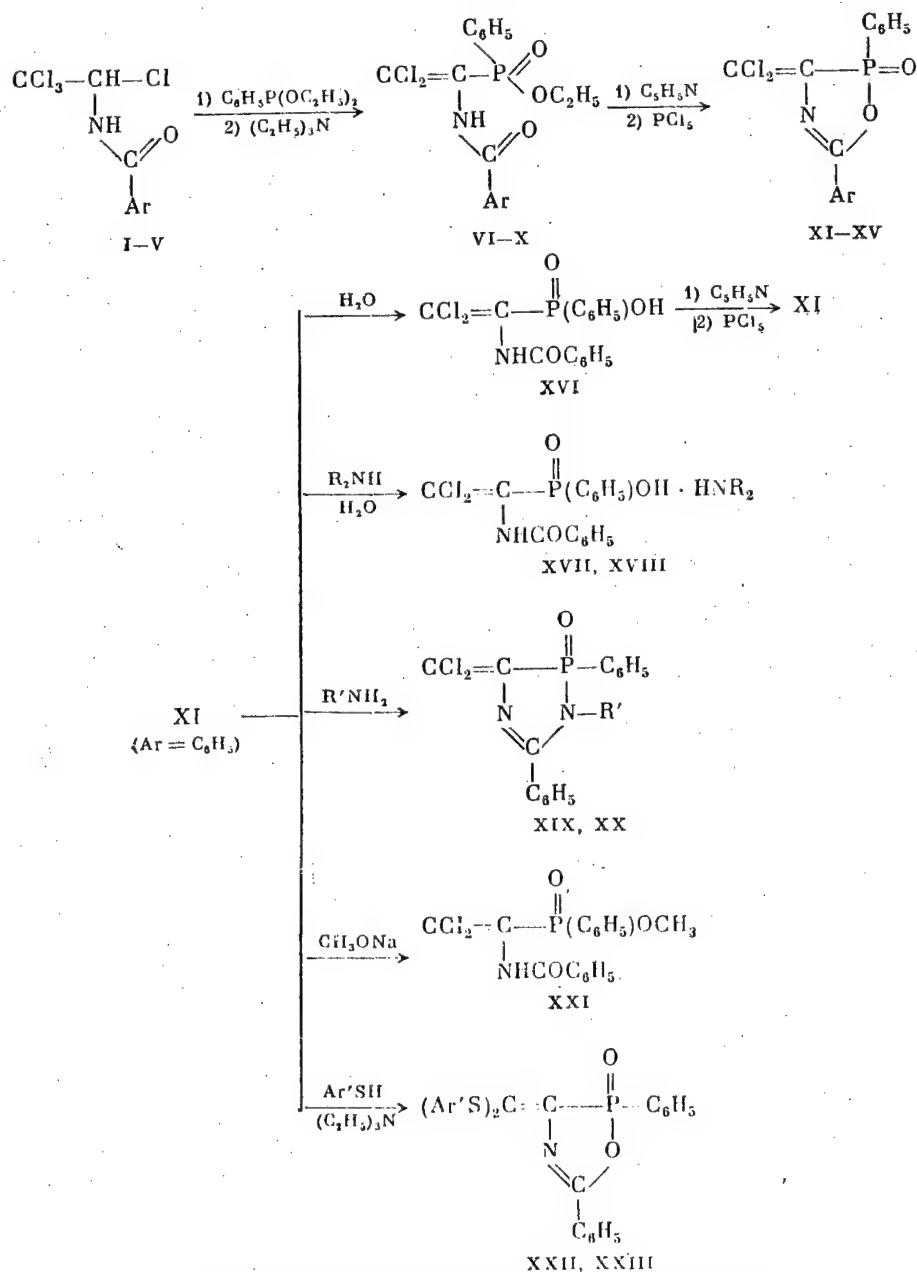
[Abstract] Methods of classical and oscillographic polarography are used to study electroreduction on a dropping mercury electrode in dimethylformamide of mixed ligand complexes of the type $\text{cis-}[M\{P(OR)_3\}_2]$, where $M=\text{Pt(II)}, \text{Pd(II)}$, $R = \text{CH}_3, \text{C}_2\text{H}_5, \text{iso-C}_3\text{H}_7$, $X = \text{Cl}^-, \text{Br}^-, \text{SCN}^-$, and also the complexes $[\text{Pt}\{P(\text{iso-C}_3\text{H}_7\text{O})_3P(\text{CH}_3\text{O})_3\}(\text{SCN}^-)_2]$ and $\text{K}_2(\text{PdCl}_4)$. It was found that mixed ligand trimethyl phosphite complexes of palladium (II) that contain halide ions and thiocyanate ions, according to data of polarography in DMF, dissociate, entering into a reaction of ligand exchange with the solvent. Complexes of composition $[\text{Pt}\{P(\text{iso-C}_3\text{H}_7\text{O})_3\}_2X_2]$, where $X = \text{Cl}^-, \text{Br}^-, \text{I}^-$, are fairly resistant to the solvating action of DMF and do not dissociate with formation of halide complexes. They are reduced on a dropping mercury electrode with formation of a single polarographic wave. Platinum (II) complexes of composition $[\text{Pt}\{P(\text{iso-C}_3\text{H}_7\text{O})_3\}_2X_2]$, where $X = \text{Cl}^-, \text{Br}^-, \text{I}^-$, are more stable in DMF solutions than their palladium counterparts, which shows up in the cathodic shift of potentials of the half-waves of the complexes, and agrees with the data in the literature. The nature of the halide ion has an effect on the ease of electric discharge of platinum complexes. The cathodic shift of potentials of the half-waves conforms to the sequence $\text{Cl}^-, \text{Br}^-, \text{I}^-$. Figures 5; references 7: Russian.

AZLACTONS OF (2,2-DICHLORO-1-ACYLAMIDOVINYLPHENYLPHOSPHINIC ACIDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 47, No 9, Sep 77 pp 1994-1999
manuscript received 27 Apr 76

DRAGH, B. S. and LOBANOV, O. P., Institute of Organic Chemistry, Academy of Sciences UkrSSR

[Abstract] It is shown that a previously developed method for producing azlactons of N-acylated α -aminoalkenylphosphonic acids is also applicable to N-acyl derivatives of α -aminophosphonic acids.



Ar = C₆H₅, n-CH₃C₆H₄, n-CH₃OC₆H₄, n-ClC₆H₄, n-NO₂C₆H₄;
R₂N = (CH₃)₂N, O(CH₂)₂N; R' = C₆H₅CH₂, C₆H₅; Ar' = n-ClC₆H₄, n-CH₃C₆H₄.

Azlactons of 2,2-dichloro-1-acylamidovinyl)phenylphosphinic acids which are synthesized by treating the corresponding ethylphosphinates with phosphorus pentachloride in the presence of pyridine, readily undergo acid hydrolysis, and are also readily broken down by highly basic secondary amines and sodium alkoxides. The interaction of these azlactons with primary amines does not stop with the formation of the usual cleavage products, but leads to derivatives of 4-dichloromethylen-5-oxo-5-phospha-2-imidazolines. In contrast to sodium alkoxides thiophenols in the presence of triethylamine do not split phosphorylated azlactons, but rather replace the chlorine atoms in the compounds in agreement with the Pearson principle. References 9: 7 Russian, 2 Western.

USSR

UDC 541.122.3+547.241

THERMOCHEMICAL INVESTIGATION OF THE BASICITY OF NEUTRAL ORGANOPHOSPHORUS EXTRACTANTS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 47, No 9, Sep 77 pp 1989-1993
manuscript received 4 Aug 75

ZARUBIN, A. I., ROZEN, A. M., and VOLNUKHINA, A. V.

[Abstract] The heats of reaction of tributyl phosphate, diisoamyl methylphosphonate, butyldibutylphosphonate and trioctyl phosphine oxide with anhydrous nitric acid in carbon tetrachloride were measured. Comparison measurements were done with trioctyl amine in carbon tetrachloride, and also with anhydrous tetrabutylammonium nitrate to determine the basicity of the nitrate ion. Triphenylphosphorus oxide and tetrabutylammonium nitrate are insoluble in carbon tetrachloride, so measurements for these compounds were done in dichloroethane. It was found that the first heats of reaction of these bases correlate satisfactorily with the electronegativities of the substituents associated with the phosphorus, with the sums of induction constants, and with the sums of Kabachnik induction constants (except for triphenylphosphorus oxide). The addition products formed when nitric acid reacts with these bases show properties of basicity. The heats of addition of the second HNO_3 molecule become more exothermal with increasing basicity of the initial base. Tetrabutylammonium nitrate also shows considerable basicity (compared with that of diisoamyl methylphosphonate). Figures 4; references 7: 4 Russian, 3 Western.

DETERMINATION OF THE BASICITY OF PHOSPHORIC ACID AMIDES BY THE METHOD OF ENTHALPIMETRIC TITRATION

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 47, No 9, Sep 77 pp 1985-1989
manuscript received 4 Aug 75

ZARUBIN, A. I., YAKSHIN, V. V., and VOLNUKHINA, A. V.

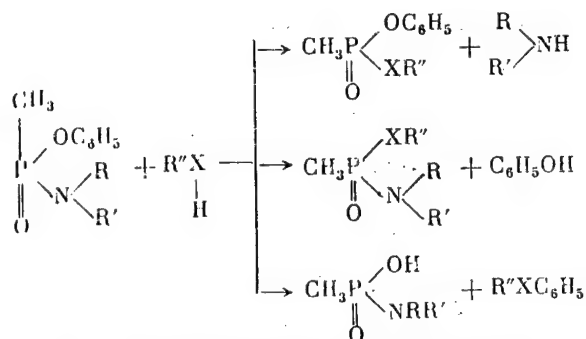
[Abstract] An enthalpimetric titration technique was used to study the process of protonation of phosphoric acid alkylamides $(C_4N_9NH)_n(C_4H_9O)_{3-n}P=O$ ($n = 0, 1, 2, 3$) with anhydrous nitric acid in a solution of carbon tetrachloride and dichloroethane. The main properties of these derivatives were determined by comparison of the enthalpies of their reaction with HNO_3 in the corresponding organic solvents. It was found that tris(alkylamides) of phosphoric acid are among the strongest of basic phosphoryl derivatives. It is suggested that in amidophosphates, the nitrogen of the amide groups associated with the phosphorus may participate as a second reaction site in the process of nitric acid protonation of these compounds. References 8: 5 Russian, 3 Western.

INTERACTION OF METHANEPHOSPHONIC ACID AMIDE ESTERS WITH NUCLEOPHILIC REAGENTS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 47, No 9, Sep 77 pp 1981-1985
manuscript received 15 Apr 76

ZAVLIN, P. M. and SHEK, V. M., Leningrad Institute of Motion Picture Engineers

[Abstract] Alkyl(aryl)amides of phenyl methanephosphonate are reacted with alcohols and amines to determine the relative pi-donor capacity of the amide and ester groups to pi bonding with the tetracoordinated phosphorus. The following possible paths of the reaction had to be considered.



$\text{R}''\text{X} = \text{C}_{10}\text{H}_{21}\text{O}, \text{C}_6\text{H}_{13}\text{NH}, \text{C}_6\text{H}_5\text{NH}, \text{HOCH}_2\text{CH}_2\text{NH}.$

Investigation of these reactions showed that nucleophilic substitution takes place at the tetracoordinated phosphorus atom in all cases. Thus it is chiefly the alkyl(aryl)amide group that undergoes substitution. References 6: Russian.

USSR

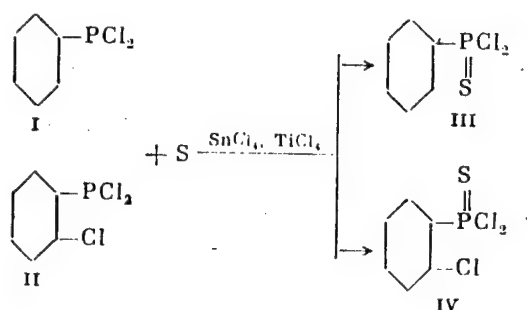
UDC 547.341.07(088.8)

ADDITION OF ELEMENTAL SULFUR TO CYCLOHEXYL- AND 2-CHLOROCYCLOHEXYLDICHLOROPHOSPHINES CATALYZED BY LEWIS ACIDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 47, No 9, Sep 77 pp 1979-1981
manuscript received 29 Oct 75

AL'ZOPA, T. G. and SUMINOV, S. V.

[Abstract] The principal method of synthesizing alkylthiophosphonic acids $RPSCl_2$ is by addition of elemental sulfur to alkyldichlorophosphines $RPCl_2$. The authors investigated addition of elemental sulfur to cyclohexyldichlorophosphine (I) and 2-chlorocyclohexyldichlorophosphine (II).



The Lewis acids used as catalysts were SnCl₄ and TiCl₄. Taking AlCl₃ and ZnCl₂ as comparison catalysts, the activity of the series declines SnCl₄ > TiCl₄ > AlCl₃ > ZnCl₂. The influence that the nature of the Lewis acid has on the addition of sulfur to 2-chlorocyclohexyldichlorophosphine (120°C, 2 hours, 0.75 mol.% catalyst) can be seen from the following data:

Catalyst	SnCl ₄	TiCl ₄	AlCl ₃	ZnCl ₂
Degree of conversion, %	95.0	84.0	18.0	7.0

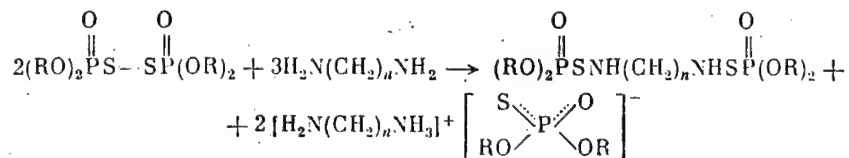
It is shown that catalytic addition of sulfur takes place with opening of the ring at the strong -S-S- bond in a reaction of type $B^+ + S_8 \rightarrow B - S_7 - S^+$, and the reason that weaker Lewis acids are better catalysts is explained in terms of the HSAB [hard and soft acids and bases] principle. After the ring in the cyclooctasulfur molecule is opened by an electrophilic metal polyhalide molecule, a complex of type $-S^+\delta - (S_6) - S - M^-\delta Cl_n$ is formed. This complex has Lewis acid properties, but is a softer Lewis acid, and reacts with the $RPCl_2$ (a soft base), giving it the final sulfur atom. References 12: 10 Russian, 2 Western.

INTERACTION OF BIS(DIALKOXYPHOSPHORYL)DISULFIDES WITH ALIPHATIC DIAMINES, AND SOME CHEMICAL TRANSFORMATIONS OF THIOPHOSPHORYLSULFENE-N-AMINOALKYLAMIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 47, No 9, Sep 77 pp 1977-1978
manuscript received 13 Feb 76

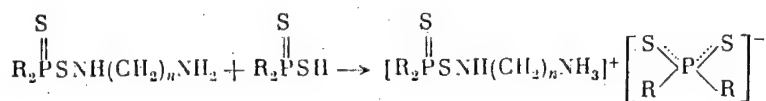
TORGASHEVA, N. A., KHASKIN, B. A., and MEL'NIKOV, N. N., All-Union Scientific Research Institute of Chemical Reagents for Plant Protection

[Abstract] Previous research by the authors showed that reaction of bis-(dialkoxy-, diaryloxythiophosphoryl- and diarylthiophosphoryl)disulfides with aliphatic diamines leads to formation of the corresponding thiophosphorylsulfene-N-aminoalkylamides and bis(thiophosphorylsulfen)alkylenediamides. In this work bis(dialkoxyphosphoryl)disulfides were treated with aliphatic diamines. The disulfides react readily with alkylenediamines at room temperature to form bis(phosphorylsulfen)alkylenediamides.



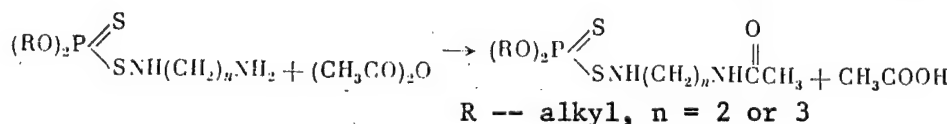
R -- alkyl, n = 2 or 3.

Thiophosphorylsulfene-N-aminoalkylamides readily yield salts with dithiophosphoric acids without destruction of the sulfenamide structure



R -- alkoxy group, n = 2 or 3

These compounds are also readily acylized with acetic anhydride to form the corresponding N'-acyl derivatives in an exothermal reaction.



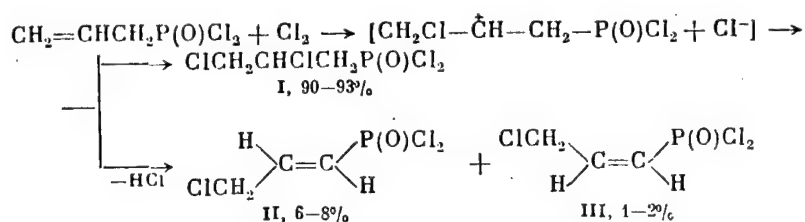
Thus the reactivity of thiophosphorylsulfene
Thus the reactivity of thiophosphorylsulfene-N-aminoalkylamides is close to that of diamines of the aliphatic series, which can be attributed to the considerable distance between the functional amino group and the sulfur and phosphorus atoms. References: 1 Russian.

HALOGENATION OF UNSATURATED PHOSPHONATES. REACTION OF 2-ALKENEPHOSPHONIC ACID DICHLORIDES WITH CHLORINE

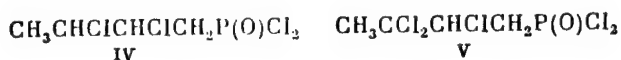
Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 47, No 9, Sep 77 pp 1970-1976
manuscript received 31 Dec 75

SHEKHADE, A. M., IGNAT'YEV, V. M., ZAKHAROV, V. I., and IONIN, B. I., Leningrad Technological Institute imeni Lensovet

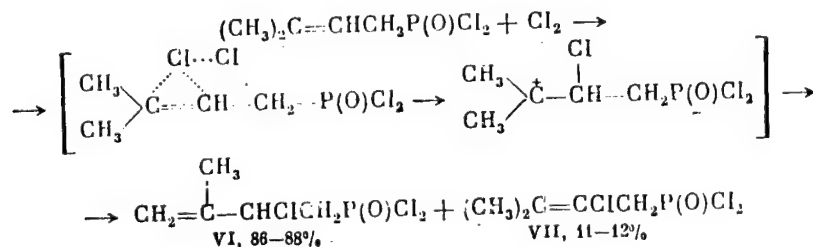
[Abstract] A study was made of the interaction of 2-alkenephosphonic acid dichlorides with chlorine. Dichlorides of 2-propene-, 2-butene-, 3-chloro-2-butene-, 3-methyl-2-butene and 4-chloro-2-methyl-2-butenephosphonic acids were investigated. Reacting 2-propenephosphonic acid with chlorine leads mainly to the addition product -- 2, 3-dichloropropanephosphonic acid dichloride (I), as well as small amounts of the dichlorides of 3-chloro-E- and -Z-1-propenephosphonic acids (II and III).



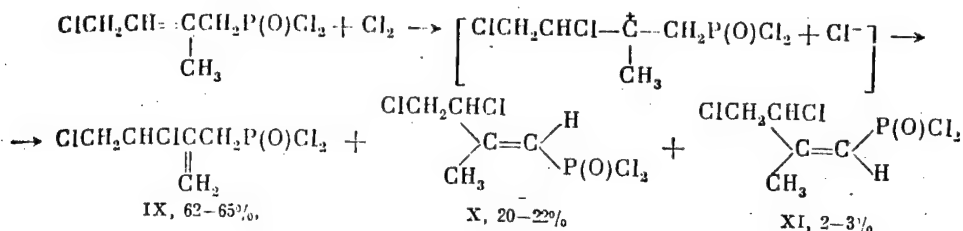
Apparently the formation of compounds II and III is due to the high mobility of hydrogenatoms of the methylene group under the influence of the phosphonic group. Chlorination of the dichlorides of 2-butene- and 3-chloro-2-butenephosphonic acids also gives addition products (IV, V).



Chlorination of 3-methyl-2-butenephosphonic acid dichloride yields 2 isomeric unsaturated phosphonates (VI and VII).



Chlorination of 4-chloro-2-methyl-2-butenephosphonic acid dichloride leads to formation of only unsaturated compounds.



The resultant dichlorides are colorless liquids that are stable in the absence of moisture. The results of the study show that chlorination of 2-alkenephosphonic acid dichlorides leads to the addition of chlorine to the double-bond or is accompanied by the release of hydrogen chloride with formation of unsaturated compounds. The structure of the latter conforms to a heterolytic reaction mechanism and is determined by the structure of the intermediate carbonium ion. Figures 5; references 15: 13 Russian, 2 Western.

USSR

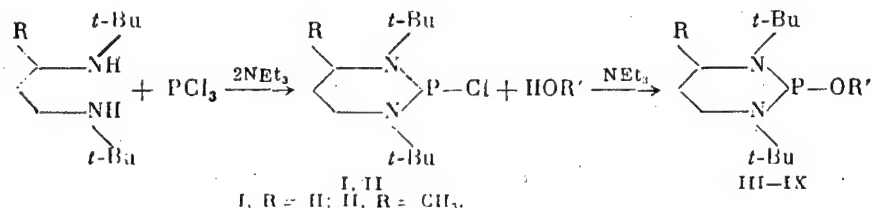
UDC 547.26'118

1,3,2-DIAZAPHOSPHORINANES. I. SYNTHESIS AND STEREOCHEMISTRY OF 1,3-DI-TER-BUTYL-1,3,2-DIAZAPHOSPHORINANES

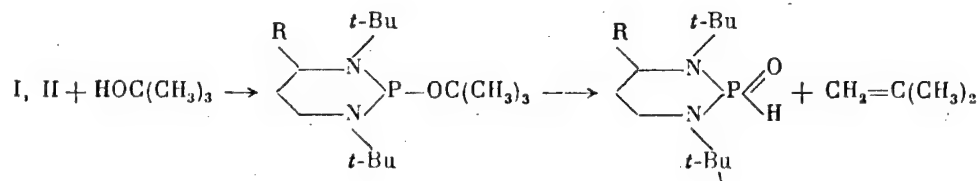
Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 47, No 9, Sep 77 pp 1960-1970
manuscript received 26 Jan 76

NIFANT'YEV, E. YE., ZAVALISHINA, A. I., SOROKINA, S. F., BORISENKO, A. A., SMIRNOVA, YE. I., and GUSTOVA, I. V., Moscow State Pedagogical Institute imeni V. I. Lenin, Moscow State University imeni M. V. Lomonosov

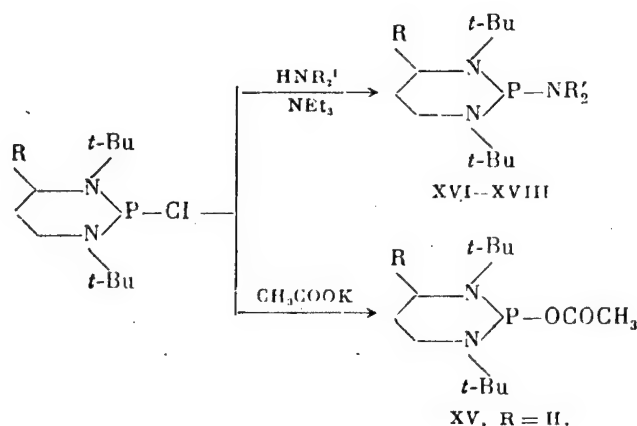
[Abstract] A study was made of the synthesis and stereochemistry of 1,3,2-diazaphosphorinanes, selection and synthesis of the initial compounds, determination of the possibility of the existence of geometric isomers, and the analysis of structural and spectral correlations. The work is based on symmetric and asymmetric derivatives of 1,3,2-diazaphosphorinanes with ter-butyl radicals associated with the nitrogen atom. A number of previously unknown amide esters were synthesized on the basis of 1,3-propylene and 1,3-butylene 1,3-di-ter-butylidiamidophosphorous acid chlorides (I) and (II).



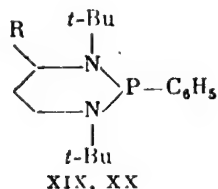
The resultant esters are oils that are distilled under vacuum and have high chromatographic mobility on aluminum oxide. They are readily oxidized and add sulfur to form the corresponding phosphates and thiophosphates (X-XIV). Acid chlorides (I, II) react anomalously with butyl alcohol.



The same compounds (I, II) can be used to synthesize amidoacetylphosphites (XV). The first representatives of 2-amido-1,3,2-diazaphosphorinanes (XVI-XVIII) were synthesized by reacting acid chlorides (I, II) with dimethylamine and ethyleneimine.



The individual product could not be isolated when diethylamine was used, probably because phosphorylation is reversible in this case, or because of space factors. Reacting phenyldichlorophosphine with 1,3-di-ter-butyl-1,3-propylene and 1,3-butylenediamines leads to formation of cyclic diamides of phenylphosphonous acid (XIX, XX).



Analysis of NMR data shows that the principal isomer is the cis-isomer in geometrically isomeric esters of 1,3-butylenediamidophosphorous acids with tert-butyl radicals associated with the nitrogen atom. References 17: 6 Russian, 11 Western.

SOLVATING CAPACITY OF PHOSPHORYL-CONTAINING COMPOUNDS WITH RESPECT TO TERT-BUTYLATES OF LITHIUM AND POTASSIUM IN 1,2-DIMETHOXYETHANE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 47, No 9, Sep 77 pp 1956-1960 manuscript received 2 Feb 76

OSIPENKO, N. G., PETROV, E. S., RANNEVA, YU. I., TSVETKOV, YE. N., and SHATENSHTEYN, A. I., Physicochemical Institute imeni L. Ya. Karpov, Moscow

[Abstract] A previous paper by these authors was devoted to a study of the influence of the structure of phosphoryl-containing compounds on their ability to solvate cations of lithium and potassium. This influence was determined from the change in the H⁻ function of a solution of ter-butoxide in ter-butyl alcohol caused by adding the phosphoryl-containing compound to this solution. However, it was found that in a proton-donor medium the pattern of solvating capacity may also depend on the formation of hydrogen bonds by the phosphoryl-containing compounds with the solvent. In this paper a tracer technique is used to study the influence that additives of the same substances have on the protophilic properties of ter-butylates in an aprotic solvent -- 1,2-dimethoxyethane. The solutions were prepared by adding measured amounts of ter-butoxides, phosphoryl-containing compounds and tracers to a pre-determined volume of 1,2-dimethoxyethane. The spectral analysis was based on the carbanion characteristics of the tracers. Measurements of the tracer ratios showed that the protophilic properties of ter-butylates of lithium and potassium in 1,2-dimethoxyethane increase considerably in the presence of solvating additives of phosphoryl-containing compounds. The influence that the structure of phosphoryl-containing compounds has on their solvating capacity in 1,2-dimethoxyethane as in ter-butyl alcohol is determined mainly by three factors: the nucleophilicity and spatial accessibility of the phosphoryl group, and also the presence of additional centers of solvation in substituents associated with the phosphorus atom. The contribution of nucleophilicity of the phosphoryl group to solvation in an aprotic solvent is somewhat higher than in a proton-donor solvent, which can be attributed to a lack of specific interaction of the solvating additive with the solvent in the former case. The ability of compounds to coordinate with the lithium cation decreases in the series $(\text{CH}_3)_3\text{PO} > (\text{CH}_3)_2\text{SO} > (\text{CH}_3)_3\text{PS}$. Figures 2; references 12: 8 Russian, 4 Western.

INFRARED SPECTRA AND ASSOCIATION OF PHOSPHORYLATED PYRAZOLINES AND PYRAZOLES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 47, No 9, Sep 77 pp 1948-1955
manuscript received 6 Feb 76

ISLAMOV, R. G., KHUSAINOVA, N. G., TIMOSHINA, T. V., POMINOV, I. S., and
PUDOVIK, A. N., Kazan' State University imeni V. I. Ul'yanov-Lenin

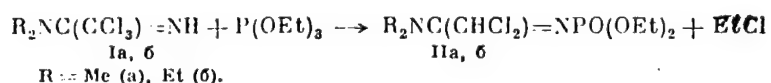
[Abstract] An investigation was made of the infrared spectra of phosphorylated pyrazolines and pyrazoles synthesized by cyclic addition of diazoalkanes to allenyl and proninylphosphonates. The spectra were recorded on the UR-10 and UR-20 instruments. The crystalline specimens were studied both as suspensions in mineral oil and as thin films on transparent substrates of CCl_4 and CH_3CN solutions. It was found that in the crystal phase and in concentrated solutions, phosphorylated pyrazolines and pyrazoles are completely associated through intermolecular hydrogen bonding. In acid and basic solvents auto-associates are destroyed and heteroassociates are formed. The strength of auto-associates is determined by the acid and basic properties of phosphorylated pyrazolines and pyrazoles. The introduction of electron-donor substituents is conducive to a rise in the basicity factor, while adding electron-acceptor substituents raises the acidity factor. The increase in strength of the intermolecular hydrogen bonding and the tendency toward auto-association in phosphorylated pyrazolines and pyrazoles as compared with unphosphorylated analogs is caused by an increase in the basicity factor with the addition of phosphoryl substituents. Figures 3; references 12: 10 Russian, 2 Western.

PHOSPHONATE-PHOSPHATE REGROUPING WHEN SODIUM DIETHYL PHOSPHIDE IS REACTED WITH BENZALDEHYDE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 47, No 9, Sep 77 pp 2156-2157
manuscript received 15 Nov 76

PUDOVIK, A. N., KONOVALOVA, I. V., ZIMIN, M. G. and SOBANOV, A. A., Kazan' State University imeni V. I. Ul'yanov-Lenin

[Abstract] Equimolar amounts of sodium diethyl phosphide and benzaldehyde were reacted in ether at 20-50°C. The following products were separated by column chromatography: diethyl hydrobenzyl phosphonate, trans-stilbene, diethylbenzyl phosphate and diethylphosphoric acid.



First, direct addition of sodium diethyl phosphide to benzaldehyde takes place. Sodium derivative (I) undergoes phosphonate-phosphate rearrangement with formation of diethyl benzyl phosphate. Anion (II) reacts with a second benzaldehyde molecule to form stilbene oxide which with sodium diethyl phosphide gives stilbene and diethylphosphoric acid. The final stage is PO-alkenation. Thus, although alpha-hydroxybenzyl phosphonates cannot be converted directly to phosphates, rearrangement occurs when sodium salts of dialkyl phosphites are reacted with benzaldehyde. References 4: 3 Russian, 1 Western.

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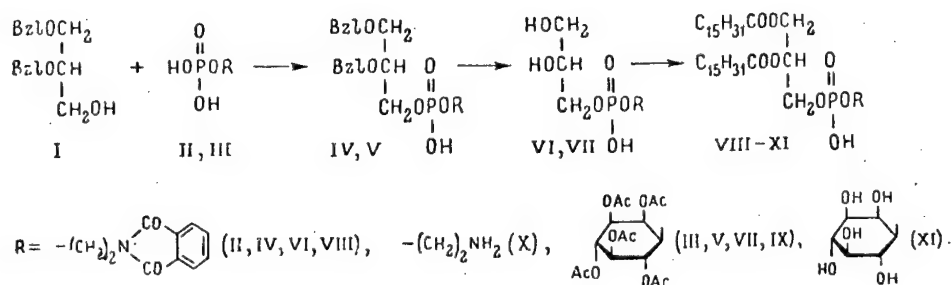
UDC 549.917

RESEARCH IN THE AREA OF COMPLEX LIPIDS. SYNTHESIS OF PHOSPHATIDYL ETHANOLAMINE AND PHOSPHATIDYL INOSITOL BY DIRECT ACYLATION OF GLYCEROPHOSPHATES WITH FATTY ACID ANHYDRIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 47, No 9, Sep 77 pp 2130-2136
manuscript received 9 Apr 76

SUKHANOV, V. A., SERGOVSKAYA, N. L., SHVETS, V. I. and YEVSTIGNEYEVA, R. P.,
Moscow Institute of Fine Chemical Technology imeni M. V. Lomonosov

[Abstract] A method for synthesizing diester glycerophospholipids is described that is suitable for producing spin-tagged and unsaturated phosphoglycerides. The phosphodiester structure of the phospholipids is formed by the method of condensing agents, acylation being preceded by phosphorylation. The phospholipids synthesized in this work were 0-(1,2-di-O-palmitoylglycero-3-O-phosphoryl)ethanolamine (X) and 1(3)-O-(1,2-di-O-palmitoylglycero-3-O-phosphoryl)-sn-myo-inositol (XI).



The reactions of production of phosphodiester derivatives (IV, V) were carried out in pyridine in the presence of 2,4,6-triisopropylbenzenesulfonyl chloride (TPS), the components being taken in a proportion of phosphate (II, III):alcohol (I):TPS=1:2:3. The dibenzyl derivatives (IV, V) were isolated from the reaction mass by chromatography on silica gel. Catalytic hydrolysis



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STEREOCHEMISTRY OF THE REACTION OF ACYLATION OF PHOSPHORUS SELENOACIDS

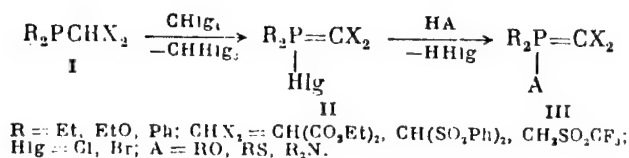
BUINA, N. A., SIBGATULLINA, F. G., GINIATULLINA, M. A., and NURETDINOV, I. A.,
Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzova, Kazan'
Affiliate of the Academy of Sciences USSR

$$\begin{array}{c} \text{R} \\ \diagup \\ \text{RO} \text{---} \text{P} \text{---} \text{Se} \\ \diagdown \quad \diagup \\ \text{OH} \quad \text{OH} \end{array} + \text{R}'\text{COBr} + \text{B} \longrightarrow \begin{array}{c} \text{R} \\ \diagup \\ \text{RO} \text{---} \text{P} \text{---} \text{Se} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{O} \end{array} \text{C} \begin{array}{c} \text{O} \\ \parallel \\ \text{---} \text{R}' \end{array} + \text{B} \cdot \text{HBr} \quad \begin{array}{c} \text{I} \\ \text{II} \end{array}$$

$\text{R} = \text{C}_2\text{H}_5; \text{R}' = \text{CH}_3, \text{C}_6\text{H}_5.$

USSR

[Abstract] It was found that phosphines R_2PCHX_2 (I) having electronegative substituents associated with the α -carbon atom react with carbon tetrahalides to form ylids with the halide atoms associated with phosphorus (II).



Reacting ylids (II) with alcohols, amines and thiols produces ylids (III).
References 5: Russian.

USSR

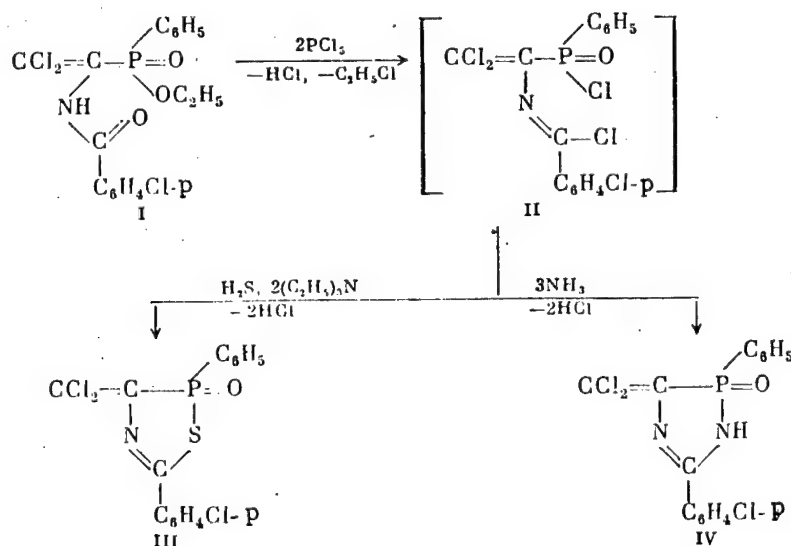
UDC 547.79+547.241

PHOSPHONYL ANALOGS OF SUBSTITUTED 5-THIAZOLONS AND 5(4)-IMIDAZOLONS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 47, No 9, Sep 77 pp 2158-2159
manuscript received 6 Dec 76

DRACH, B. S. and LOBANOV, O. P., Institute of Organic Chemistry, Academy of Sciences UkrSSR

[Abstract] The first representatives of phosphonyl analogs of substituted 5-thiazalons and 5(4)-imidazolons were synthesized.



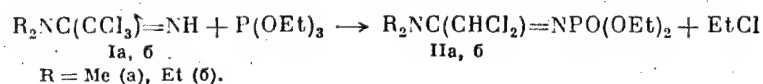
Although N-substituted p-chlorobenzimide chloride (II) could not be isolated in pure form, the synthesis was proved by the 5-phenyl-2-p-chlorophenyl-4-dichloromethylen-5-oxo-5-phospha-2-thiazoline (III) and 5(4)-phenyl-2-p-chlorophenyl-4(5)-dichloromethylen-5(4)-oxo-5(4)-phospha-2-imidazoline (IV) obtained from the crude product of the reaction of enamide (I) with phosphorus pentachloride. References 3: Russian.

PHOSPHORYLATION OF AMIDINES. REACTION OF N,N-DIALKYL TRICHLOROACETAMIDES WITH TRIETHYL PHOSPHITE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 47, No 9, Sep 77 pp 2157-2158
manuscript received 25 Nov 76

SHEVCHENKO, V. I., KAL'CHENKO, V. I. and SINITSIA, A. D., Institute of Organic Chemistry, Academy of Sciences of the UkrSSR

[Abstract] N-acylchloralimines having carboxylic and phosphoric acid groups react exothermally with trialkyl phosphites to form products of C- and N-phosphorylation. The authors found that N,N-dialkyltrichloroacetamides (I) which contain the less polarized azomethyne group in the $\text{CCl}_3=\text{N}-$ group react with triethyl phosphite with much more difficulty to form N-phosphorylated dichloroacetamides (II). The reaction is of the Perkov type and is accompanied by transfer of a proton.



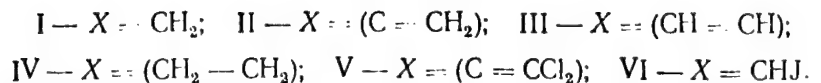
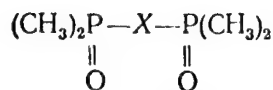
References 2: Russian.

CONFORMATIONAL ANALYSIS OF DIOXIDES OF TETRAMETHYLVINYLDENE-, -VINYLENE-, -ETHYLENEDIPHOSPHINES AND SOME OF THEIR HALIDE DERIVATIVES IN CONNECTION WITH THE PROBLEM OF SELECTIVITY OF COMPLEX FORMATION.

Kiev TEORETICHESKAYA I EKSPERIMENTAL'NAYA KHIMIYA in Russian Vol 13, No 4, Jul/Aug 77 pp 488-495 manuscript received 29 Aug 76

BARANOV, A. P., DASHEVSKIY, V. G., MEDVED', T. YA., and KABACHNIK, M. I., Institute of Organoelemental Compounds, Academy of Sciences USSR, Moscow

[Abstract] In a previous paper the authors described the method of calculation, parametrization and the results of theoretical conformational analysis of tetramethylmethylenediphosphine dioxide (I). This paper gives the results of an investigation of the conformational possibilities of other diphosphine dioxides: tetramethylvinylidenediphosphine (II), cis-vinylene-diphosphine (III), -ethylenediphosphine (IV), -dichlorovinylidenediphosphine (V) and -iodomethylenediphosphine (VI).



The conformational energies of these compounds are calculated within the framework of the additive method of interatomic interactions. On the assumption that these compounds are bidentate ligands when bound with alkali metal cations, the authors calculate the distance between donor atoms corresponding to the low-energy regions of conformational maps. The selectivity of complex formation is determined from the results. Figures 8; references 10: 7 Russian, 3 Western.

USSR

UDC 547.241;541.127

THE APPLICATION OF HAMMETT'S EQUATION WITH GENERAL KABACHNIK CONSTANT TO THE STUDY OF SULFUR VULCANIZATION OF RUBBER WITH TRIS(ORGANOAMIDO)-PHOSPHATES

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY--KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA in Russian Vol 20, No 8, 1977 pp 1207-1210 manuscript received 16 Nov 76

RATNIKOVA, T. V. and GINAK, A. I., Leningrad Technological Institute imeni Lensovet

[Abstract] A correlation between the consumption rates of free sulfur during the vulcanization of natural rubber with tris-(aryl-, monoalkyl-, dialkyl-amido)phosphates (TAP) and the general Kabachnik constants has been achieved. The TAPs have been shown earlier to be effective accelerators of rubber vulcanization. Specifically, the following TAPs were used: tris(anilido-, m-, p-toluidido)phosphates, tris(n-butyl-, i-butyl-, tert-butyl, n-hexyl-, n-octyl-, n-dodecyl-, dimethyl-, diethyl- and n-dibutylamido)phosphates. The kinetics of free sulfur consumption was studied in crude rubbers and in vulcanized products obtained at 120-140° (in 5-20 min) with 80 mmoles S₈ or 60 mmoles TAP and 80 mmoles S₈ per liter of the mixture. The results of the analysis have shown that TAPs exhibit nucleophilic properties in the sulfur vulcanization reactions, being electrophilically attacked by sulfur through a transitional state of low polarity. Keeping in mind the high complex forming ability of TAP, one can assume that the reaction of TAP with sulfur occurs via formation of molecular complexes. Figures 2; references 13: 10 Russian, 3 Western.

USSR

UDC 541.69:542.91:547.1'118

REACTION OF O-ETHYL-O-(β -ALKYLMERCAPTOETHYL)-CYCLOHEXYLPHOSPHONATES AND THEIR METHYL IODIDES WITH CHOLINESTERASES

Moscow IZVESTIYA AKADEMII NAUK--SERIYA KHIMICHESKAYA in Russian No 7, Jul 77
pp 1606-1609 manuscript received 16 Apr 76

GODOVIKOV, N. N., AGABEKYAN, R. S., KUZAMYSHEV, V. M., BERKHAMOV, M. KH., ZAKHAROVA, L. M., PEGOVA, Z. K., and KABACHNIK, M. I., Institute of Organo-metallic Compounds, Academy of Sciences USSR

[Abstract] Inhibitory activity of O-ethyl-O-(β -alkylmercaptoethyl)cyclohexyl-phosphonates and their methiodides towards butyrylcholinesterase and acetylcholinesterase was studied showing that they react as reversible inhibitors. The inhibitory activity increases with increasing length of alkyl radical connected to the sulfur atom. Table 1; figures 2; references 5: 4 Russian, 1 Western.

USSR

UDC 615.285.7.033.77.015.4

SASINOVICH, L. M., OVSYANNIKOVA, L. M., and BADAYEVA, L. N., Institute of Hygiene and Toxicology of Pesticides, Polymers, and Plastics, Kiev

TOXICITY OF NEW, CHEMICALLY DISTINCT, PESTICIDES ABSORBED PER CUTEM

Moscow GIGIYENA TRUDA I PROFESSIONAL'NYYE ZABOLEVANIYA in Russian No 7, 1977
pp 34-36

[Abstract] Albino rats, rabbits, and guinea pigs were used to investigate the toxic effects of epicutaneously applied pesticides (2000 mg/kg single application or 20 applications of 100 mg/kg). Of 36 new pesticides under investigation, high toxicity was demonstrated by the following organophosphorus compounds (OPC): phosvel (LD₅₀ 50mg/kg), acaricide-228F (LD₅₀ 611 mg/kg), cyanox (LD₅₀ 2010 mg/kg), and bromophos (LD₅₀ 2820 mg/kg). OPC induced an intense inflammatory process in the liver reflected by hypoproteinemia, elevated serum activities of alanine- and aspartate aminotransferases, reduced liver RNA concentration, 20-75% depression in serum and liver cholinesterase activities, and a decrease in alkaline phosphatase activity. Chlororganic pesticides induced marked histopathologic changes in the liver, heart, and kidneys. Serum activities of the enzymes in question were increased by 52-230%, while hepatic activities were depressed by 17-73%. Derivatives of carbamic and dithiocarbamic acids induced dysproteinemia (125% increase in total proteins) and elevation in serum urea (by 130%). Cholinesterase and alkaline phosphatase activities were unaffected. Urea derivatives induced changes similar to, but less pronounced than those due to chlororganic compounds. Derivatives containing nitro groups stimulated synthesis of enzymes involved in transamination but did not lead to a change in the serum protein pattern; however, the hematopoietic system was adversely affected. Tables 1; references 3: Russian.

ON THE POSSIBILITY OF ESTABLISHING MAXIMUM PERMISSIBLE LEVELS FOR SUBSTANCES THAT ARE DANGEROUS IN CONTACT WITH THE SKIN

Moscow GIGIYENA TRUDA I PROFESSIONAL'NYYE ZABOLEVANIYA in Russian No 7, 1977
pp 29-33

SHASHKINA, L. F., Branch of the All-Union Pharmaceutical Chemistry Research
Institute imeni S. Ordzhonikidze, Kupavna, Moscow Oblast

[Abstract] In determining maximum permissible exposure to hazardous substances consideration must be given to the efficiency with which toxic agents are absorbed by the skin. Recent studies at enterprises involved with androgenic hormones have demonstrated that contamination of unprotected skin (palms; $0.01-0.04 \text{ mg/cm}^2$) may exceed by an order of magnitude protected skin areas ($0.004-0.0055 \text{ mg/cm}^2$) and lead to increased libido among male workers and ovarian dysfunction and virilism among the female staff. Such findings resulted in excluding women from work involving androgenic hormonal preparations. In view of the findings that testosterone, methyltestosterone, and other testosterone derivatives show high androgenic potency despite a relatively slow rate of cutaneous absorption (0.147% of applied dose in 12 h), experimental studies were conducted with methyltestosterone applied to a 4 cm^2 area of skin of rats for 4 months (0.1 and 0.05 mg/kg). Extrapolation of the results led to the conclusion that 0.001 mg/cm^2 represents the maximum permissible level of skin contamination with methyltestosterone, which was in relatively good agreement with the value of 0.005 mg/cm^2 deemed to be without serious consequences in male workers. Tables 2; references 21: 17 Russian, 4 Western.

USSR

UDC 613.632.4+614.718):628.511/514

CORRELATION ANALYSIS OF METHODS FOR DETERMINING THE EFFECTIVENESS OF FILTERS FOR THE STERILIZATION OF AIR

Moscow KHIMIKO-FARMATSEVTICHISKIY ZHURNAL in Russian No 9, Sep 77 pp 128-132
manuscript received 25 Jan 77

BATOVA, L. K., MOTINA, G. L., All-Union Scientific Research Institute of Antibiotics

[Abstract] A detailed comparison was made of the transmission coefficients of oil mists, aerosols of bacteria, and methylene blue dye through eight different types of filtering materials. The average hydrodynamic diameter of the fibers contained in the filters ranged from 1 to 26 microns. A direct correlation was obtained between the transmission coefficients for Staph. aureus vs. both the oil mist and the methylene blue dye. This approach reduces the number of tests which must be run in order to evaluate the effectiveness of a filter material for a particular application. References 6: Russian.

USSR

UDC 628.543.1

FROM THE WORK EXPERIENCE ON A SANITATION-EPIDEMIOLOGICAL STATION IN MYTISHCHI

Moscow VODOSNABZHENIYE I SANITARNAYA TEKHNIKA in Russian No 9, 1977 pp 31-32

MOROZOVA, G. A., Sanitation Epidemiological Station in Mytishchi

[Abstract] Based on an example of a large machine building plant in Mytishchi, the activity of a sanitation supervision unit has been reviewed, noting successful technological solutions to the sewage purification problem at that plant. Until 1964 there were no purification units at the plant, except for primitive oil traps. In 1971 a 10 year plan was developed for construction of a sewage plant system and a purification station. Special collectors were installed for the spent oil to prevent its disposal into the sewage system. Oil regeneration units were built; the non-recyclable oil was used for fuel. A special unit was built to remove chromium salt impurities from the recyclable material. As a result the once heavily polluted river running by the plant became much cleaner.

USSR

OPTIMIZATION OF DESIGN SOLUTIONS IN THE AREA OF SANITATION TECHNOLOGY

Moscow VODOSNABZHENIYE I SANITARNAYA TEKHNKA in Russian No 9, 1977 pp 20-23

BOGUSLAVSKIY, L. D., MINZHURDORZH, L. (MISI (?) IMENI V. V. KUYBYSHEV),
PAVLYUCHUK, A. I., Belorussian Polytechnical Institute, and STRAZHNIKOV, A. M.,
Main Housing Administration Mosgorispolkom

[Abstract] A given design solution is considered to be optimal when capital investment for the end product is at a minimum; however, this situation is not always practical because of design or technological restrictions. Cost analysis usually leads to a range of acceptable solutions rather than a single optimum. It is concluded that in the process of deciding on optimization of designs, one should not be limited by determination of the optimum point only. In many cases transition from one optimal solution to a range of possibilities makes it possible to improve the effectiveness of the solution under real conditions. Three cases are analyzed in support of the above.

USSR

UDC 628.511

PROTECTION OF THE AIR FROM DUST DURING UNLOADING OF BULK MATERIALS

Moscow VODOSNABZHENIYE I SANITARNAYA TEKHNKA in Russian No 7, 1977 pp 30-32

BOBROVNIKOV, N. A., Leningrad Railroad Engineering Institute imeni V. N. Obraztsov

[Abstract] The process of unloading bulk materials from rail cars by tipping the cars, as currently performed, involves the pollution of the surrounding air with large quantities of dust, as entrained air billows upward from the pile of material, carrying with it dust particles over a significant area. The Railroad Engineering Institute has developed dust reduction devices based on aspiration and filtering of air from the railroad car-tipping area, capable of greatly reducing the dust content of the air. A method is suggested for determining the air. A method is suggested for determining the air flow rate necessary to reduce the dust content in the air to the level called for by the hygienic norms. References 2: Russian.

USSR

UDC 628.336.004.8

CONSERVATION OF THE ENVIRONMENT AND UTILIZATION OF WASTE WATER PRECIPITATES

Moscow VODOSNABZHENIYE I SANITARNAYA TEKHNIKA in Russian No 7, 1977 pp 27-28

YEVILEVICH, A. Z., All-Union Scientific Research Institute for Hydrolysis,
Leningrad

[Abstract] By 1980, municipal sewage in the USSR will reach a volume of 50 million cubic meters per day, to which must be added 5 times the amount of industrial liquid effluent. Adding rain water runoff from these same two classes of sources, the total quantity of sediment in waste water will be 100 million tons per year. The question of utilization of the sludge which can be recovered from waste water has not been fully developed; essentially, no one is in charge of this development. Whereas the purity of water discharged from treatment plants is carefully regulated and inspected, there is a vacuum of leadership in the area of possible recovery of valuable raw materials from the sludge and other solid products generated by these plants. The trend toward zero-waste operation of production facilities based on modern scientific and technological progress provides unlimited possibilities for improvement of the environment and improvement of the national economy.

USSR

UDC 628.52/.53:628.51:697.9

STRUGGLE WITH HARMFUL EMISSIONS OF CHEMICAL FIBER PLANTS

Moscow VODOSNABZHENIYE I SANITARNAYA TEKHNIKA in Russian No 7, 1977 pp 22-24

MENIS, V. B., All-Union Scientific Research Institute for Planning of
Synthetic Fiber Plants

[Abstract] Artificial and synthetic fiber plants can act as sources of large quantities of harmful emissions into the atmosphere. This article reviews some of the steps which have been taken in recent years to reduce the emissions of these plants, including not only basic restudy of the principles of ventilation, but also the design of the actual equipment and apparatus used to produce chemical fibers in order to isolate processes, recycle effluents, recover useful chemicals formerly lost into emissions and convert extremely harmful effluents into less harmful forms by such processes as burning and oxidation. The chemical fiber industry is intensively studying ventilation techniques in order to reduce air pollution. Since more air passes through the human body than either water or food in a day's time, it is obvious that pure air is the most important and irreplaceable consumer product. References 3: Russian.

METHOD FOR CALCULATING THE LEVEL OF POLLUTION OF THE ATMOSPHERE

Moscow VODOSNABZHENIYE I SANITARNAYA TEKHNICA in Russian No 7, 1977 pp 19-22

NIKITIN, V. S., MAKSIMKINA, N. G., PLOTNIKOVA, L. V., and SAMSONOV, V. T.,
Central Scientific Research Institute for Organization of Labor; All-Union
Council of Trade Unions

[Abstract] An analytical formula was developed at the Institute for calculating the level of air pollution between factory buildings when low-level sources of pollution are present, that is based on a study of the wind flow characteristics around a group of industrial buildings of simple shape and approximately equal height. Analysis of the formula shows that in general the level of air pollution in the second and subsequent spaces between buildings is determined as the sum of three concentrations: that created by low-level sources; the background level from the existing space between buildings; and the background level of the incoming air at the factory complex. The background concentrations created by the low sources of emission in upwind zones between buildings may be greater than the background level in the incoming air at the factory. The article calls for a single standard document for calculating the level of pollution of the air in industrial areas and adjacent residential zones when both high and low sources of emissions are present. References 6; Russian.

PREDICTION OF POLLUTION OF THE GROUND LAYER OF THE ATMOSPHERE

Moscow VODOSNABZHENIYE I SANITARNAYA TEKHNICA in Russian No 7, 1977 pp 15-18

EL'TERMAN, V. M., Central Scientific Research Institute for Industrial
Building

[Abstract] Several suggestions are presented which may be used to develop a unified method for calculating pollution of the ground level of the atmosphere, which encompasses all types of sources of emission. The first problem is to define what constitutes a low-level source, as influenced by the distortion of the air stream around a building, and what constitutes a high-level source of pollution for which surface turbulence can be ignored. Some sources, such as those located in the mixing zone but venting their effluent upward at some velocity, may be either "low" or "high" sources, depending on wind velocity and other factors. A classification of emission sources is suggested and conditions are established under which the maximum concentration of harmful substances can be expected in the lowest layer of the atmosphere. A constant of "dangerous" wind velocity is defined and formulas presented for its calculation. It is demonstrated that it is now possible to develop a single method for the calculation of the dispersion of

harmful substances and for technical-economic selection of optimal engineering decisions to assure protection of the atmosphere from pollution. References 8: Russian.

USSR

UDC 628.52/.53:628.51:697.9

THE SPREAD OF TECHNOLOGICAL AND VENTILATION EMISSIONS IN THE ATMOSPHERE

Moscow VODOSNABZHENIYE I SANITARNAYA TEKHNKA in Russian No 7, 1977 pp 12-14

TITOV, V. P., and TISHKIN, V. S., Moscow Construction Engineering Institute

[Abstract] The Moscow Construction Engineering Institute is developing a general approach to the problem of predicting the pollution of the air by gaseous emissions, which reflects the three-dimensional nature of the process and the changes of the characteristics of velocity and turbulence exchange factors throughout the volume being studied. A possibility is provided for considering the effect of dynamic and gravitational forces. The method allows a single methodological basis to be used to calculate the dissipation of harmful impurities from both technological and ventilation sources, and from both high stack and low-level sources. All three dimensions of buildings are considered in determining the parameters defining the intensity of diffusion of impurities. Considering the effect of the aerodynamics of flow around a building by a stream of air on the plume of effluent, as well as dynamic and gravitational forces, allows the problem of determining the most dangerous wind speed and the problem of optimization of atmospheric emissions to be addressed. References 6: Russian.

USSR

UDC 614.7:632.92

ESTIMATION OF THE POPULATION DOSE AND OF THE RELATIVE POSSIBILITY OF DELAYED CONSEQUENCES OF THE USE OF PESTICIDES IN AGRICULTURE

Moscow GIGIYENA I SANITARIYA in Russian No 9, Sep 77 pp 81-87 manuscript received 10 Mar 76

LIKHTAREV, I. A., USHAKOVA, A. P. [deceased] and MOISEYEV, A. A., Leningrad Scientific Research Institute of Radiation Hygiene, Ministry of Health RSFSR, Chair of Radiation Energy, Central Institute of Doctors' Specialization, Ministry of Health USSR

[Abstract] Studies have shown that 90% of all pesticides entering the human organism do so with food products, and the remaining 10% with air and water.

An attempt has been made to develop a mathematical model for the migration of pesticides and their accumulation in the human organism. As an indicator of potential danger of the utilization of pesticides in agriculture, the authors used a new concept of "cumulative population dose of pesticides," a value which combines the integral contact time of the population exposed to the pesticide, the aging of the population and some metabolic constants for such a period. Formulas have been derived to determine this population dose, and for the transmission of pesticides through the environment, contamination of the food resources and accumulation in the human organism. Although mathematical expressions were derived, some of the concepts used could not really be measured by practicing specialists in the field at this time. The authors believe that a "cumulative population dose of pesticides" should be developed for the entire USSR and the difficulties which may be encountered in reaching a practical solution should be solved by the specialists working in the respective fields. References 7: 6 Russian, 1 Western.

USSR

UDC 614.71-036.8

EFFECTIVENESS OF THE MEASURES TAKEN TO PROTECT THE ATMOSPHERE IN THE REGION
AFFECTED BY INDUSTRIAL DISCHARGES IN DONETSK

Moscow GIGIYENA I SANITARIYA in Russian No 9, Sep 77 pp 87-89 manuscript
received 21 Dec 76

GALUSHKO, A. P., GRIN', N. V., SOLOV'YEV, V. I., RUDCHUK, Z. YA., and
MIROSHNICHENKO, V. YU., Donetsk Municipal and Regional Sanitation-
Epidemiological Station, Donetsk Medical Institute

[Abstract] Considerable effort has been exerted to improve the air quality over Donetsk, but the determination of the effectiveness of all the measures taken has been hampered by the diversity of non-specific emission sources. Industrial plants are interspersed with the residential areas. To complicate matters further, the laboratory lacked adequate equipment for its task. Only during the last year was the necessary equipment secured, doubling the analytical potential. In spite of these difficulties, some zonal analyses were carried out identifying the most serious sources of contamination: the cement-asphalt plants, the non-ferrous plants, stag cotton plant, coke-chemical plant, the Donetsk plant of chemical reagents, etc. All of these plants reduced emissions into the atmosphere by introducing better filters, changing to a cleaner fuel, sealing leaking equipment and even substituting some starting or intermediate reagents. All of these measures lowered the contamination of the atmosphere by the following values: dust - 40%, sulfur dioxide - 20%, phenol - 12% and carbon monoxide - 36%.

USSR

UDC 614.7:632.95:007

A CYBERNETIC ASPECT OF THE PROBLEM OF PREVENTION OF ENVIRONMENTAL CONTAMINATION WITH PESTICIDES

Moscow GIGIYENA I SANITARIYA in Russian No 9, Sep 77 pp 14-16 manuscript received 11 Jan 77

SPYNU, YE. I. and IVANOVA, L. N., All-Union Scientific Research Institute of the Hygiene and Toxicology of Pesticides, Polymers and Plastics, Ministry of Health USSR

[Abstract] An attempt was made to analyze the pesticide-human environment biological system encompassing the phenomena of cumulative effects, thresholds, retentions, various multiple factors and their linear and non-linear relationships. To control all of this it is necessary to limit the introduction of pesticides into the human organism by all routes so that the maximum permissible levels are not exceeded. Currently, the solution of the totality of this problem is not possible. Attention must be given to complex sub-systems: pesticide-plants, pesticide-soil, pesticide-air and pesticide-water. At this stage practical solutions for the system pesticide-plant have been reported. A structural schematic has been proposed for the administration of a program for the safe use of pesticides. Figures 2; references 7: all Russian.

USSR

UDC 635.21:632.35

TOXIC EFFECT OF CHEMICAL PREPARATIONS ON THE PATHOGENS OF BLACK STALK AND POTATO GANGRENE

Moscow KHIMIYA V SEL'SKOM KHOZYAYSTVE in Russian Vol 14, No 7, 1977 pp 52-53

DOROZHNIKIN, N. A., and BEL'SKAYA, S. I., Institute of Experimental Botany, Academy of Sciences Belorussian SSR, POPOV, F. A., and GENERALOVA, I. V., Belorussian Scientific Research Institute of Potato, Vegetable and Fruit Growing

[Abstract] In laboratory experiments it has been shown that the antibiotics Bronokot and Kasumin, as well as the fungicides Topsin, NF-65 and Cyneb, showed high bactericidal activity against the black stalk pathogen. Against the pathogen of potato gangrene, fungicidal activity was exhibited by TMTD, BMK, Cyneb and Benamyl. To control dry and damp rot of potato tubers, agents exhibiting both fungicidal and bactericidal activity should be selected. This can be achieved by concurrent application of both types of these reagents. No figures, references 3: all Russian.

USSR

UDC 632.954:633.15

AGELON AND LINURON ON CORN FIELDS

Moscow KHIMIYA V SEL'SKOM KHOZYAYSTVE in Russian Vol 15, No 7, 1977 pp 57-60

NEPOCHATOV, A. P., Grakov Experimental Field

[Abstract] Although there is a wide selection of herbicides for the control of weeds on corn fields with rather good results, many agents show narrow applicability range and some are even harmful to the corn plants. The effectiveness of Agelon and Linuron in weed control on corn fields was studied during the 1970-1974 period in the Kharkov region - an area of fertile chernozem of the Southern Ukraine forest-steppe. Agelon is a suspension of 33.3% atrazine and 16.7% premetrine. It is most effective against annual grassy weeds and dicotyledons in doses of 3-4 kg per hectare. Fields infested with annual dicotyledonous weeds can also be treated effectively with Linuron at a rate of 6 kg per hectare, the agent being applied prior to preplanting soil cultivation. Linuron's phytotoxicity depends to a large degree on the mineral content in soil. Both Agelon and Linuron show no undesirable properties towards corn when applied prior to preplanting soil cultivation even at doses of 8 kg per hectare. No figures, references 6: all Russian.

USSR

UDC 632.954:633.34

TREFLAN ON SOYBEAN FIELDS

Moscow KHIMIYA V SEL'SKOM KHOZYAYSTVE in Russian Vol 15, No 7, 1977 pp 60-62

VESELOVSKIY, I. V., SKURYATIN, N. YE., and ZHEREBKO, V. M., Ukrainian Agriculture Academy

[Abstract] Treflon was field-tested in 1972-74 on the Ukrainian forest-steppe chernozem as a weed controlling agent on soybean fields. The agent was highly effective against weeds in the dose range 1.7-5.1 kg/ha. At doses of up to 2.6 kg/ha, Treflon showed no effect on the soybean plants; at higher doses plant thinning of up to 32.3% took place. The yield of the beans increased by 44.6-70% in comparison to unweeded control fields. For the area studied, the optimal dose of Treflon for chemical weeding of soybean fields appeared to be 2-2.5 kg/ha. No figures, references 8: all Russian.

USSR

UDC 632.954:635.25

THE USE OF HERBICIDES ON ONION FIELDS IN LIGHT OF AGROTECHNICAL PROCEDURES

Moscow KHIMIYA V SEL'SKOM KHOZYAYSTVE in Russian Vol 15, No 7, 1977 pp 65-69

ZHUKOVA, P. S., Belorussian Scientific-Research Institute of Potato, Fruit and Vegetable Growing

[Abstract] Field tests were performed in the 1970-74 period on the experimental farm "RUSINOVICH," in search for the most effective herbicide for the control of weeds on onion fields. The following have been identified as effective agents against mono- and dicotyledonous weeds on the turf-podzol, medium agrilaceous soil of Belorussia: Ramrod at 5 kg per ha, Dactal at 10/ha, Prometrin at 1.5/ha and Ramrod combined with Prometrin at 5 + 1 kg/ha. These agents destroyed up to 80-96% of weeds and 26-37% of their seeds in the top layer of the soil. Additional preplanting cultivation of the soil saves about 25 man-days per hectare, normally wasted in manual weeding. Nutritional balance of the soil and the onion crop was not affected by using these herbicides. The products store well. No figures; references 6: 5 Russian, 1 Western.

USSR

UDC 543.063:632.95

CHROMATOGRAPHIC BEHAVIOR OF HERBICIDES OF THE PHENYLUREA GROUP AND CARBOXYLIC ACID ANILIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 47, No 9, Sep 77 pp 2051-2053 manuscript received 13 May 76

KLISENKO, M. A. and PIS'MENNAYA, M. V.

[Abstract] As a basis for environmental monitoring of residual amounts of herbicides of phenylurea derivatives and carboxylic acid amides, the behavior of individual representatives of these groups was studied under conditions of adsorption chromatography in a thin layer as a function of the influence of substituents, the nature of the adsorbent, and the nature of the carrier. Twenty-five derivatives of phenylurea and carboxylic acid anilides were separated on aluminum oxide and silica gel. A table is given that summarizes the R_f values for these herbicidal compounds for the following carriers: chloroform, benzene, ethyl ether, benzene:acetone = 9:1, chloroform:acetone = 95:5, carbon tetrachloride:ethyl ether = 1:1 and hexane:acetone = 5:3. The mobility of the compounds on the chromatograms is determined mainly by their specific reaction with the active centers on the surface of the sorbent and by the way that this reaction is influenced by electron shifts due chiefly to substituents associated with the carbon atom of the carbonyl group. References 4: Russian.

USSR

UDC 632.954:633.34

HERBICIDES FOR THE PROTECTION OF SOYBEAN

Moscow KHIMIYA V SEL'SKOM KHOZYAYSTVE in Russian Vol 15, No 9, 1977 pp 34-36

OSKAPEV, V. I., GUREYEVA, M. P., AGEYEV, V. P., and MIKHALEVA, V. P., Ryazan Agricultural Experimental Station

[Abstract] Under adverse conditions of extensive weed growth, the crop of the soybean seeds drops considerably. A number of herbicides has been evaluated during the period of 1973-1974 at the Ryazan experimental station in an attempt to find optimal combinations of the herbicidal agents for the soybean fields. It was established that Linuron at a dose of 1.5 kg per hectare, Prometrin at 2 to 2.5 kg per hectare, Dactal at 15 kg per hectare and Ramrod at 4 kg per hectare were the most effective agents. The first two were also the most economical agents. They showed no toxic effects to the soybean plants.

USSR

UDC 632.951:634.25

INSECTICIDES FOR THE CONTROL OF EASTERN PEACH LEAF-ROLLER MOTH

Moscow KHIMIYA V SEL'SKOM KHOZYAYSTVE in Russian Vol 15, No 9, 1977 p 56

ZAGAYANYI, S. A., IGNATOVA, YE. A., and GUR'YAN, I. S., Scientific Research Institute of High Altitude Horticulture and Floriculture

[Abstract] Field studies have shown that the following agents are effective insecticides for the control of Grapholitha molesta busck. in subtropic areas: Bromophos, Phozalon, Phtalophos and Chlorophos. These agents break down rather rapidly showing no persistent residual levels in the fruits a week to 10 days after the application of the agent. Although effective, Sevin is not recommended for this application because of its retention in the fruit for over a one month period. References 2: both Russian.

USSR

UDC 632.954.633.491

LINURON AND DACTAL APPLIED ON POTATO FIELDS DURING IRRIGATION

Moscow KHIMIYA V SEL'SKOM KHOZYAYSTVE in Russian Vol 15, No 9, 1977 pp 57-60

SHESTOPALOVA, N. A., Dnepropetrovsk Vegetable-Melon Experimental Station

[Abstract] The main reason for the poor crop on the irrigated potato fields was the excessive weed infestation. Chemical weeding removed the weeds at a rather low cost of labor and funds. Field studies have shown that Linuron (2-4 kg per hectare) and Dactal (4-12 kg per hectare) are very effective in controlling the weeds on potato fields, including such specimens as prickly grass and common amaranth pigweed. Up to 60-99% of the weeds were destroyed. There were no undesirable effects noted on the quality or the quantity of the potatoes harvested. References 8: all Russian.

USSR

UDC 632.951:633.31

INSECTICIDES FOR THE PROTECTION OF ALFALFA SEEDS

Moscow KHIMIYA V SEL'SKOM KHOZYAYSTVE in Russian Vol 15, No 9, 1977 p 55

NAYDENOV, G. P., Ukrainian Scientific Research Institute of Irrigation Agriculture

[Abstract] Tychius flavus and Brucnophagus roddi are two of the most destructive pests of alfalfa seeds in the southern Ukraine, being responsible for destruction

of up to 6-12% of these seeds. A number of insecticides was evaluated in 1972-1975. Phozalon, Benzophosphate, Thiodan, Bazudin and Metaphos were the best agents for the control of the above insects. The insecticides should be applied twice: first just prior to blooming, and then again after the blooming period. The second spraying should be done with less toxic agents such as Phozalon or Thiodan.

USSR

UDC 621.892.093:62-82

FIRE RETARDANT NONTOXIC LIQUIDS FOR HYDRAULIC SYSTEMS

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 7, 1977 pp 55-58

SUKHOTIN, A. M., KAZANKINA, A. F., ZARETSKAYA, L. V., NECHAYEVA, T. N.,
BERDENIKOV, A. I., and VODOP'YANOVA, V. A.

[Abstract] The properties of fire retardant nontoxic hydraulic liquids -- FHL are presented. These liquids consist of glycerine, water soluble polymer, water, and various additives for the improvement of anticorrosive, antiwear and antifoaming properties. Changing the brand of the setting agent and of the contents of various components, makes it possible to obtain liquids differing considerably in viscosity and satisfying a number of technical requirements. These liquids are designed for use in hydraulic systems instead of the flammable oils. Experimental results are reported on the analysis of hydraulic liquids. Tables 5; references 8: 5 Russian, 3 Western.

USSR

UDC 628.162.048

TRENDS IN THE IMPROVEMENT OF THE TECHNOLOGY OF PURIFICATION OF NATURAL WATERS FOR INDUSTRIAL WATER SUPPLY

Moscow VODOSNABZHENIYE I SANITARNAYA TEKHNIKA in Russian No 10, 1977 pp 5-9

APEL'TSIN, I. E., PROSHIN, E. A., PAVLOV, G. D., All-Union Scientific Research Institute for Water Supply, Sewer Systems, Hydraulic Engineering Structures and Engineering Hydrogeology, and FAYLOND, M. SH., Ukrainian Water and Sewage Planning Commission

[Abstract] The two institutes represented by these authors have developed a plan for a water treatment station for production of process water with a new arrangement of components, and new types of reagents and filter charging materials. The purpose of this design work was to determine optimum improvement at low cost to treat and process water, by eliminating suspended sediment in natural water for use in industrial enterprises. Approaches used include regeneration of coagulant from the sediment and dewatering of secondary sediment. Cost reductions in comparison to present designs of 5-20% are expected. The use of a cationic flocculant in place of aluminum or iron salt coagulants can further reduce adjusted costs by 22-27% and overall water treatment costs by 40-50%. The use of powdered reagents added "dry," or of concentrated reagent solutions, multiple action mixtures, and flocculation chambers as well as coarse-grained filters with high sludge capacity are considered promising. Figures 3; table 1; references 5: 3 Russian, 2 Western.

USSR

UDC 628.06.04

DETERMINATION OF MAXIMAL SALT CONCENTRATION DURING EVAPORATION OF SEA WATER

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY--KHIMIYA I KHIMICHESKAYA TEKHNLOGIYA in Russian Vol 20, No 6, 1977 pp 842-845 manuscript received 9 Jul 76

DYABLO, V. V., KRICHEVSKAYA, YE. L., KAGANSKIY, I. M., and MIKHAYLOVA, N. V., Chair of the Technology and Automation of Chemical Productions, Odessa Polytechnical Institute

[Abstract] A method has been developed for calculating maximum concentrations of salts during evaporation of sea water on thermal demineralization equipment. The calculation was carried out on the basis of data showing water contents at the junction points of solubility graph of the system $\text{Na}^+, \text{Mg}^{2+} || \text{Cl}^-, \text{SO}_4^{2-} + \text{H}_2\text{O}$. The calculated results agreed well with experimental data obtained by the visual-polythermal method. For a sample of Caspian Sea water, the function was calculated to be $C_{\text{max}} = 278 + 0.293 t \cdot \text{g/kg}$. Figures 2; references 6: all Russian.

USSR

UDC 621.592 + 621.642.002.2

TRENDS IN THE DEVELOPMENT OF CRYOGENIC HELIUM EQUIPMENT

Moscow KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian No 7, 1977
pp 5-8

KALITIN, P. P., PRON'KO, V. G., and DAVYDENKO, I. A.

[Abstract] Planned production of cryogenic devices in the tenth five-year plan is summarized to point out the need for advances in quantity, efficiency, dependability and level of automatization of helium equipment. Specific cryogenic helium devices are considered. The prospects for more effective limits of cooling below the widely accepted throttling level. A central feature of most devices of the "Geliymash" enterprise is the use of turbine reduction valves of high frequency as a source of cold. Methods are presented for improving operation through procedures that increase pressure and stability, and permit rotor speeds of up to 400,000 rpm. Problems related to transportation and further research, development and design are discussed. Figures 3; references 6: 5 Russian, 1 Western.

USSR

UDC 621.351

POSSIBLE MEANS OF PRODUCING HYDROGEN AND OXYGEN FROM WATER FOR PURPOSES OF HYDROGEN POWER PRODUCTION

Moscow ELEKTROKHIMIYA in Russian Vol 13, No 11, Nov 77 pp 1611-1615 manuscript received 1 Oct 75

BAGOTSKIY, V. S., VOL'FKOVICH, YU. M., GOLIN, YU. L., SUVOROV, A. N., and SHERSTOBITOV, YU. S., Institute of Electrochemistry, Academy of Sciences, USSR

[Abstract] An analysis is presented of possible means for producing hydrogen and oxygen from water in closed cycles. An attempt is made to systematize the various trends in research relating to the so-called hydrogen power economy, grouping them by methods of oxygen production: 1) thermal decomposition of the oxides of metals and metallides; 2) electrochemical reactions; 3) decomposition of water with halogens; 4) sulfuration roasting of oxides; and 5) chlorination roasting of oxides. It is suggested that electrochemical reactions in chemical sources of power and in electrolyzers can facilitate certain stages of the cycle. Thermodynamic criteria are presented from which it is possible to select the most promising cycles. Table 1; references 15: 11 Russian, 4 Western.

USSR

USE OF A FLUIDIZED BED IN THE PROCESS OF GASIFICATION OF SOLID FUEL UNDER PRESSURE

KHIMIYA TVERDOGO TOPLIVA in Russian No 4, Jul/Aug 77 pp 115-116

CHERNENKOV, I. I., SHAFIR, G. S., and GAVRILOVA, A. A., Institute of Mineral Fuels

[Abstract] One progressive trend in the area of gasification of solid fuel is the combination of a fluidized bed with high pressure. This method allows solution of a number of problems related to the creation of a highly productive process for gasification of solid fuel. The author's institute has developed a high-intensity method of gasification of coal in a fluidized bed under pressure, as well as high temperature elimination of mechanical impurities and compounds of sulfur from the gas. A pilot-scale installation has been built, operating at 30 atm. gauge. The maximum productivity of the installation is 1,000 m³ (stp)/hr. Experiments on gasification of coal at pressures of 5 and 10 atm. gauge have been conducted and the results are presented in tabular form. The gas produced is 95% sulfur free.

USSR

KINETICS OF FORMATION OF PYROCARBON DURING THERMAL DECOMPOSITION OF METHANE

KHIMIYA TVERDOGO TOPLIVA in Russian No 4, Jul/Aug 77 p 64

ROGAILIN, M. I., Institute of Mineral Fuels

[Abstract] A study was made of the kinetics of thermal decomposition of methane resulting in the formation of pyrocarbon on the surface of porous graphite when the influence of homogeneous reactions can be ignored. Under these conditions, and assuming that the process of formation of pyrocarbon is a result of heterogeneous thermal decomposition of methane at interface, including the chemisorption both of the initial reagent and of the reaction product, a kinetic equation was developed for the rate of formation of pyrocarbon that is based on the pyrocarbon formation rate constant, methane equilibrium sorption constant, hydrogen equilibrium sorption constant, partial pressure of methane in the gas phase, and the partial pressure of hydrogen in the gas phase. The results produced confirm the applicability of the equation to the analysis of the experimental data. The activation energies calculated indicate that the mechanism of thermal decomposition of methane passes through the stage of formation of the methylene radical and molecular hydrogen on the surface of the carbon.

USSR

UDC 62-634.002.2

INCREASING THE RESOURCES OF JET FUELS

Moscow KHIMIYA I TEKHNLOGIYA T PLIV I MASEL in Russian No 10, 1977 pp 8-12

RADCHENKO, YE. D., ROZHKOV, I. V., ENGLIN, B. A., KHOKHLACHEVA, M. V., KHAYKIN, M. D., and GUSEVA, A. V., All-Union Scientific Research Institute of the Petroleum Industry

[Abstract] Dealing with an increase of jet-fuel resources, attention is drawn to the question of increasing the resources via a rise, according to an analogy with USA specifications ASTM D 1655-74 and ASTM ES2-74, of the crystallization initiation temperature from -60 to -40 and -50°C. Data are presented on the relationship of the potential content of the jet-fuel fractions of Nizhnevar-tovskaya oil and Zapadnotebukskaya oil from the crystallization initiation temperature of these fractions. Tables 4; references 13: 9 Russian, 4 Western.

USSR

UDC 546.791.6-386

REACTION OF URANIUM HEXAFLUORIDE DISSOLVED IN ACETONITRILE WITH SULFUR CONTAINING REAGENTS

Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 22 No 10, Oct 77 pp 2793-2795 manuscript received 9 Jul 76

SEVAST'YANOV, V. G., and KOP'YEVA, M. A., Institute of General and Inorganic Chemistry imeni N. S. Kurnakov, Academy of Sciences USSR

[Abstract] Reactions of uranium hexafluoride with sulfur containing reagents was investigated in acetonitrile. The reaction leads to the reduction of uranium and formation of the following addition products: $UF_4 \cdot CH_3CN$; with hydrogen sulfide - $UF_4 \cdot 2HF \cdot 2CH_3CN$; with diethyl sulfide and ethanedithiol - $UF_4 \cdot CH_3CN$; with thiocarbamide - $UF_5 \cdot 2SC(NH_2)_2$ and with dithiooxamide - $UF_4 \cdot SC_3N_2H_5$. Acetonitrile is coordinated with uranium through the nitrogen atom. The last two compounds listed exhibited the coordination bond of uranium-sulfur. References 5: 2 Russian, 3 Western.

STUDY OF THE ORTHOPHOSPHATES OF TETRAVALENT URANIUM

Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 22 No 7, Jul 77, pp 1891-1895 manuscript received 25 Oct 76

KOBETS, L. V., KOLEVICH, T. A., and UMRYEIKO, D. S., Belorussian State University

[Abstract] The conditions for the preparation of di- and trisubstituted uranium orthophosphates were studied, as well as their thermal and spectral properties. U^{6+} was reduced by U^{4+} in a column filled with a zinc amalgam. The disubstituted phosphate was obtained by passing solutions of uranyl sulfate mixed with sulfuric and phosphoric acids through the column, and also without SO_4^{2-} anions by reducing solutions of uranyl phosphates in H_3PO_4 . Uranium (IV) phosphate was precipitated by slow dilution of a reduced solution with water. It is shown that the tetrahydrate is stable at atmospheric pressure. The areas of water vapor pressure for 2.5 hydrate and 1.5 hydrate were determined and IR spectra and thermal stability of the tetrahydrate were studied. Apparently, trisubstituted uranium orthophosphate cannot be separated from its solutions at room temperature. This is in agreement with earlier American studies. References 10: 2 Russian; 8 Western.

POLAND

REACTION OF PHOSPHITE ESTERS WITH 4-BENZYLIDENE-1,2-DIPHENYL-3,5-PYRAZOLIDINEDIONE

Warsaw ROCZNIKI CHEMII in Polish Vol 51, No 10, pp 1879-1882 manuscript received 25 Feb 77

SOLIMAN, Fouad M. and SHABANA, R., National Research Center, Dokki - Cairo, Egypt, A.R.E.

[Abstract] A study was made of the reactivity of 4-benzylidene-1,2-diphenyl-3,5-pyrazolidinedione (1) toward trialkyl phosphites, i.e.: trimethyl-, triethyl-, and triisopropyl phosphites. It was found that when red benzylidene compound 1 was allowed to react with triethyl- and triisopropyl phosphites, in ether or benzene, colorless 1:1 adducts, 3a and 3b, were formed, respectively. Their identity was verified by corrected combustion values and molecular weight determination. Compounds 3a and 3b are insoluble in aqueous sodium hydroxide and exhibit no color reaction with alcoholic ferric chloride. The reaction of 1 with trimethyl phosphite in ether yielded a colorless crystalline adduct which proved to be 0,0-dimethyl [α -(3-hydroxy-5-oxo-1,2-diphenyl-3-pyrazolin-4-yl)benzyl]-phosphonate (5). Compound 5 is soluble in aqueous sodium hydroxide and gives a color reaction with alcoholic ferric chloride solution. It is also readily methylated upon treatment with ethereal diazomethane solution to give the corresponding monoethyl ether 6. The probable mechanisms of reaction and structures of products are discussed on the basis of chemical and spectroscopic investigations. 2 structural formulas. 11 references: 1 Polish, 10 Western.

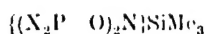
GDR

ON THE CONSTITUTION OF THE TRIMETHYLSILYL DERIVATIVES OF IMIDODIPHOSPHORYL COMPOUNDS

Leipzig ZEITSCHRIFT FUR ANORGANISCHE UND ALLGEMEINE CHEMIE in German Vol 433, No 6, Aug 77 pp 200-206 manuscript received 13 Oct 76

RIESEL, L., CLAUSSNITZER, A., RUBY, C., Chemistry Section of the Technical University, Dresden

[Abstract] A reaction of esters and dialkylamides of imidodiphosphoric acid with hexamethyldisilazane leads to the formation of trimethylsilyl derivatives. ^1H -, ^{29}Si - and ^{31}P -NMR data indicate that the trimethylsilyl group is bound to oxygen with a rapid, reversible exchange between the two phosphoryl oxygen atoms. The boiling points (K_p) and NMR data are presented in the following table:



X	Kp	$\delta^{31}P$	$\delta^{29}Si$	$\delta^1H(SiMe_3)$
OMe	85-88°C/ 10 ⁻⁴ Torr	-3,3 ppm, 14,4 ppm $J_{AB} = 54,8$		+0,22 ppm
OEt	90-93°C/ 10 ⁻³ Torr	-6,8 ppm (-2,5; -14,5; -15,8)		+0,23 ppm
OPr	110-115°C/ 5 · 10 ⁻⁵ Torr			
NMe ₂	105°C/ 10 ⁻³ Torr	+10,6 ppm	+18,7 ppm	+0,26 ppm
NEt ₂	142°C/ 10 ⁻³ Torr	+4,6 ppm; +8,3 ppm	+17,8 ppm	+0,30 ppm
NPr ₂	182°C/ 10 ⁻³ Torr	+5,0 ppm +9,0 ppm		

A detailed interpretation of these data is presented in the article.

References 17: 6 East German, 2 Russian, 9 Western.

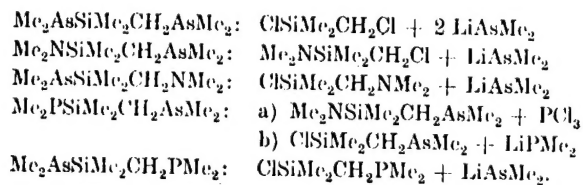
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ALTERNATE LIGANDS. IV [1, 2] PREPARATION OF CHELATING LIGANDS OF THE TYPE $Me_2XSiMe_2CH_2X'Me_2$ (Me = CH₃; X, X' = N, P AND/OR As)

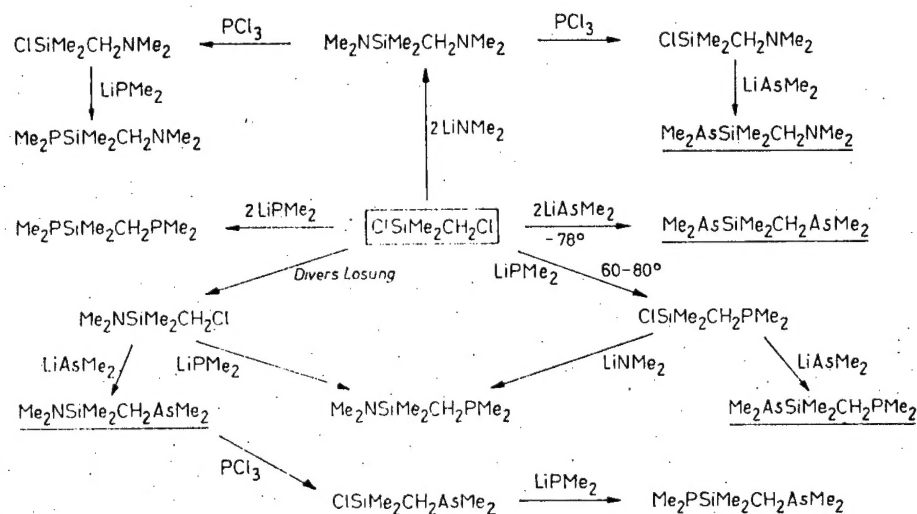
Leipzig ZEITSCHRIFT FUR ANORGANISCHE UND ALLGEMEINE CHEMIE in German Vol 433, No 6, Aug 77 pp 157-166 manuscript received 4 Oct 76

GROBE, J., and SCHEUER, G. F., Eduard-Zintl Institute of the Technical Academy, Darmstadt

[Abstract] Chelating ligands of the above general type were synthesized from $ClSiMe_2CH_2Cl$ by the following reactions:



A prerequisite for the synthesis of ligands with various donor groups is the differing reactivity of the functional groups SiCl or CCl which enable a stepwise addition of SiX or CX'. Difficulties were presented by the thermal instability of LiAsMe₂ and by metal-halogen exchange reactions. The reactions proceed according to the following scheme:



Analytical and spectroscopic methods (IR, NMR, MS) were used to characterize the new compounds. References 14: 5 East German, 9 Western.

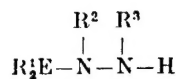
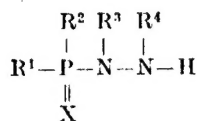
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CHEMISTRY OF HYDRAZINE AND ITS DERIVATIVES.53 [1] SYNTHESIS OF P-, As- AND Sb-SUBSTITUTED HYDRAZINES BY THE ADDITION OF P-H, As-H AND Sb-H GROUPS TO $\text{N} = \text{N}$ DOUBLE BONDS

Leipzig ZEITSCHRIFT FUR ANORGANISCHE UND ALLGEMEINE CHEMIE in German Vol 433 No 6, Aug 77 pp 119-132 manuscript received 4 Nov 76

LINKE, K. H., and BRANDT, W., Institute of Inorganic Chemistry of the University, Koln

[Abstract] By the addition of diphenylphosphinous acid, diphenylthiophosphinous acid, methyl hydrogen phenylphosphonite, diethyl hydrogen phosphite, diphenylphosphane, dibutylphosphane, diphenylarsane, diethylarsane and diphenylstibane to the $\text{N} = \text{N}$ double bond of diethyl azodicarboxylate, dimethyl azodicarboxylate, ethyl phenylazocarboxylate and azobenzene, the following P-, As- and Sb-substituted hydrazines were obtained:



	R ¹	R ²	R ³	R ⁴	X
1	C ₆ H ₅	C ₆ H ₅	CO ₂ C ₂ H ₅	CO ₂ C ₂ H ₅	O
2	C ₆ H ₅	C ₆ H ₅	CO ₂ CH ₃	CO ₂ CH ₃	O
3	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	CO ₂ C ₂ H ₅	O
4	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	O
5	C ₆ H ₅	C ₆ H ₅	CO ₂ C ₂ H ₅	CO ₂ C ₂ H ₅	S
6	C ₆ H ₅	C ₆ H ₅	CO ₂ CH ₃	CO ₂ CH ₃	S
7	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	CO ₂ C ₂ H ₅	S
8	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	S
9	C ₆ H ₅	OCH ₃	CO ₂ C ₂ H ₅	CO ₂ C ₂ H ₅	O
10	C ₆ H ₅	OCH ₃	CO ₂ CH ₃	CO ₂ CH ₃	O
11	C ₆ H ₅	OCH ₃	C ₆ H ₅	CO ₂ C ₂ H ₅	O
12	OC ₂ H ₅	OC ₂ H ₅	C ₆ H ₅	CO ₂ C ₂ H ₅	O
13	OC ₂ H ₅	OC ₂ H ₅	C ₆ H ₅	C ₆ H ₅	O

	E	R ¹	R ²	R ³
14	P	C ₆ H ₅	C ₆ H ₅	CO ₂ C ₂ H ₅
15	P	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅
16	P	n-C ₄ H ₉	CO ₂ C ₂ H ₅	CO ₂ C ₂ H ₅
17	P	n-C ₄ H ₉	C ₆ H ₅	CO ₂ C ₂ H ₅
18	As	C ₆ H ₅	CO ₂ C ₂ H ₅	CO ₂ C ₂ H ₅
19	As	C ₆ H ₅	CO ₂ CH ₃	CO ₂ CH ₃
20	As	C ₆ H ₅	C ₆ H ₅	CO ₂ C ₂ H ₅
21	As	C ₂ H ₅	C ₆ H ₅	CO ₂ C ₂ H ₅
22	Sb	C ₆ H ₅	CO ₂ C ₂ H ₅	CO ₂ C ₂ H ₅
23	Sb	C ₆ H ₅	C ₆ H ₅	CO ₂ C ₂ H ₅

Reactions 1, 5, 9, 18 and 22 have been previously reported by the authors. Addition of the P-H groups was done in benzene, methylene chloride or ether. The conditions and course of the reactions suggest a polar reaction mechanism with the exception of 15 which appears to proceed through free radical intermediates. The azo systems employed were distinctly different in their reactivity with the element-H groups used and longer heating or the addition of catalysts was necessary in some instances. Although light, air and moisture were excluded in reactions 22 and 23, an additional redox process was unavoidable and a separation from the byproducts was unsuccessful. In these cases, identification was made by mass spectral analysis alone. In all instances, the spectroscopic data are in agreement with the structural formulae presented. The values are published in five tables. References 9: 1 East German, 8 Western.

CSO: 1841

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